OPTICAL METHODS

of

CHEMICAL ANALYSIS

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PREFACE

The purpose of this book is to present a compact, abridged survey of the field of optical methods of analysis, in a style suited both to the practical analyst and to the advanced student of analytical chemistry. An attempt has been made to cover the construction, the fundamental theory, and the analytical uses of those instruments which have proved of most value to the chemist.

The author has emphasized the design and manipulation of instruments rather than the theoretical aspects of the subject, but has endeavored to present whatever theoretical considerations are necessary for intelligent application of the methods discussed. It is impossible in a book of this size to give detailed directions for the solution of every type of analytical problem. The objective has been, rather, to give enough fundamental information so that the analyst may make an intelligent choice of alternative methods, or plan a workable method to fit his particular problem. Various pitfalls are pointed out, and type procedures are described in many cases. An extensive bibliography of leading references enables the analyst to refer, when necessary, to more comprehensive works or to specific articles in recent periodicals. The references are not always to original articles, but have been selected, for the most part, on the basis of simplicity, recency, and extent of bibliography.

In the few cases where theoretical considerations do not bear directly on the practical question, as in certain phases of optical crystallography, or wherever the theory is too involved for elementary presentation, as for example in the case of absorption spectroscopy, it has been considered advisable to revert either to "working rules" or to evasions, however regrettable they may be. The physicist may well shudder at some of the resulting heresies, both of commission and omission, herein contained, but the author must plead the extenuating circumstance that this book is designed primarily for the practical analyst,

who is more concerned with analysis of his unknown than with the physical theories involved. It should be noted, however, that most of the instruments were developed by physicists or physical chemists, and that in many cases the analytical uses are consequences of broad, theoretical investigations.

The book is arranged as a text with a chapter devoted to each optical method and its uses. The form of presentation varies from chapter to chapter, according to the nature of the subject matter, and, although formal consistency is sacrificed to some extent, the author has found through experience that the arrangement given seems to be most suitable for purposes of instruction. Topics such as circular dichroism, which are of no particular importance in analytical work, are included because of their bearing on other subjects studied concurrently by the student.

A chapter on elementary crystallography has been included because conventional courses in chemistry are apt to neglect this important field. Crystallography is also a necessary prerequisite to optical crystallography, which is discussed in the following chapter. The practical utility of the latter method of analysis is now becoming widely recognized in organic chemistry, after many years of use in inorganic chemistry and mineralogy. Optical crystallography is probably the simplest of the few analytical methods which permit identification of the molecule as a whole, and it is hoped that this book will serve to introduce the possibilities of the method to those who are not familiar with its manifold uses.

The author is indebted to Professors L. F. Hamilton, A. C. Hardy, G. R. Harrison, and A. A. Morton, and Dr. J. S. Lukesh for their encouragement and valuable suggestions, and to Messrs. J. E. Tyler, E. R. Little, and K. J. Radimer for their helpful criticisms. The author is particularly grateful to Professor A. G. Woodman, his teacher and esteemed friend, whose help and encouragement have been invaluable.

THOMAS R. P. GIBB, JR.

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GENERAL CONSIDERATIONS AND NOTES ON INSTRUCTION

Students frequently regard an instrumental method of analysis with the idea "You push the button, the machine does the rest." Since the reaction that develops as they discover the falsity of this impression is apt to be discouraging, this preliminary word of warning may not be out of place. The fact of the matter is that instrumental methods, and especially micro methods, often require more painstaking technique than the macro "wet" methods with which the students are familiar. Furthermore, since the interpretation of results is more involved than in the case of wet methods, greater demands are made on the theoretical background and experience of the analyst.

The advantages of optical methods are not stressed in the chapters that follow except as they are apparent from the descriptions of the methods themselves. In general, we may say that optical methods of analysis present two principal advantages over strictly chemical methods:

Speed: Most of the methods discussed are very rapid, once the necessary preliminary operations, if any, have been performed. In many cases, results are obtained in a few minutes for determinations requiring days if carried out by conventional methods. One outstanding point is the fact that most of the methods are adaptable to continuous consecutive determinations such as are encountered in routine control work.

Sensitivity: Most of the methods are applicable to micro quantities, and the sensitivity is, in general, far greater than that of strictly chemical methods. The sensitivity of the spectrograph is proverbial, whereas that of the colorimeter, nephelometer, and fluorophotometer is not far behind. It is not uncommon to find descriptions of quantitative photometric methods sensitive to 0.01 micrograms, with an accuracy of 1 or 2 per cent. The identification of a milligram or so of crystalline material may often be accomplished by optical crystallographic means and the entire sample actually recovered unchanged.

Correlation of Optical Methods

There are many problems encountered by the practicing analyst which are not amenable to conventional methods of analysis, *e.g.*, determination of traces, analysis of small samples, and determination of complex or unstable materials. In such cases, instrumental or optical methods are *necessarily* used. On the other hand, certain analyses that *may* be performed by conventional methods are often more easily carried out through the use of special techniques, *e.g.*, determination of purity or identity, concentration of a known solute, etc. Lastly, optical methods may be used advantageously in conjunction with conventional methods of analysis either as a preliminary guide, as in the case of the spectrograph or polarizing microscope, or as a supplement, as in the case of the colorimeter and allied instruments. A classic example is the detection of adsorbed or coprecipitated material in a weighed gravimetric precipitate.

Not only may the various optical methods be correlated with conventional methods, but they may be used to supplement one another. For instance, let us assume that a few milligrams of powdered sample are brought to the analyst. Preliminary microscopic observation reveals the presence of two components, which, after optical crystallographic examination are shown to be *probably* SiO_2, $K_2Al_2(SO_4)_4$, or substances of similar optical character, together with either $ZnSiF_4$ or $CoF_2 \cdot 5HF \cdot H_2O$. Time is not spent on a complete identification by this method, but the sample is submitted to spectrographic examination, which reveals the presence of potassium, aluminum, and cobalt. Correlation of the two sets of data at once establishes the sample as a mixture of the sulfate with the cobalt salt. After suitable treatment, any one or all of the ions may be determined colorimetrically without danger of interference from unsuspected contaminants.

Notes on the Laboratory

The laboratory setup and the choice of necessary instruments for instructional purposes depend largely on the funds available and the availability of the instruments themselves. Probably the most expensive single item is the microscopic equipment, although it should be noted that it is possible to convert any stand equipped with a revolving stage into a petrographic microscope, by means of Polaroid and an improvised Becke lens.

The saving thus effected should permit the purchase of at least one standard petrographic microscope for each group of four students.

The spectrographic equipment need not be particularly elaborate, since the principles and technique may be illustrated with one of the less expensive grating spectrographs. A Spekker spectrophotometer or photoelectric instrument is desirable, but one of the methods of absorption spectroscopy mentioned in the text requires only a quartz cell in addition to the usual spectrographic equipment. Several simple microphotometers are described, which are both inexpensive and entirely satisfactory.

The number of colorimetric instruments on the market is unusually large, and the costs are not excessive. The same applies to a lesser degree in the case of refractometers, and attention should be called to a very inexpensive refractometer of novel design which has recently appeared on the market. Although this instrument is of low precision, it should be suitable for many purposes.

Polarimeters and saccharimeters that are designed for precise measurements are quite expensive, but again, there is available an inexpensive instrument employing Polaroid, which illustrates all the principles and which may be used for many of the experiments described.

The laboratory itself is best divided into four connecting rooms: A small spectrograph room, adequately ventilated, an adjoining darkroom, a polarimeter room, and a colorimeter room, which should be provided with lighttight window shades or other means of partial darkening. The fourth and largest room is reserved for work with microscopes and kindred instruments. Low workbenches which may be made from ordinary office desks, according to the description given by Chamot and Mason, are earnestly recommended. Whatever form of table is used, it should be less than 29 in. high, be equipped with several drawers, and give ample kneeroom. The worktables should not face a window or light-colored wall, nor should they have polished tops, since glare is the greatest single cause of eye fatigue in microscopy.

Notes on Instruction

The author's course is "required" of third-year students of chemistry and biology and is "elected" by students pursuing

courses in chemical engineering and other subjects. Four consecutive hours a week are devoted to laboratory work and, instead of lectures, the tutorial system is employed throughout the laboratory period. The number of instruments is such that eight students may work at one time, and a staggered schedule of experiments permits the use of fewer instruments than would otherwise be possible. Student equipment for a group of eight consists of a grating spectrograph, a prism spectroscope, a grating spectroscope (for wedge spectra), a photoelectric spectrophotometer, a Duboscq colorimeter, a neutral-wedge photometer, a photoelectric colorimeter, a turbidimeter, a polarimeter, a saccharimeter, an Abbe and a dipping refractometer, four petrographic microscopes, and one biological microscope with all accessories. Additional equipment such as balances, glassware, ovens, and a muffle furnace are, of course, provided, and facilities are also available for pH measurements, polarography, chemical microscopy, and spot tests.

The experimental details are more suggested than required, and a student is allowed a great deal of latitude in planning any given experiment. Emphasis is placed throughout on practical applications and the actual or possible uses of the methods studied.

OPTICAL METHODS
OF CHEMICAL ANALYSIS

CHAPTER I

SPECTROCHEMICAL ANALYSIS

1. The development of spectroscopy as an analytical tool
dates from the observation of Kirchhoff and Bunsen[1,*] in 1860 that
the spectra of flames colored with various salts were character-
istic of the metallic components. It was also noted that the
wave lengths of the observed lines were independent of the
temperature of the flame but that the number of observable lines
became greater as the temperature was increased.

The work of Gramont,[2] Hartley,[3] and others furthered the
development of chemical spectroscopy through the fundamental
stages, until in the early 1920's the method commenced to attract
the serious attention of analytical chemists in many fields. In
the "Index to the Literature on Spectrochemical Analysis
for 1920–1937," by Meggers and Scribner,[4] there are only 5 con-
tributions listed for 1920, 10 for 1925, 46 for 1930, and 128 for
1935.

2. Scope, Limitations, and Advantages.—The generally recog-
nized analytical uses of the spectroscope may be summarized as
follows:

1. Qualitative analysis for metallic elements and certain non-
metals, including P, Si, C, B, and As. A sample of only a milli-
gram or so is required, and the content of metal may be of the
order of 0.001 per cent or less, depending on the metal itself and
on the conditions of excitation.

2. Quantitative analysis for these metals and nonmetals in
amounts not exceeding a small percentage of the total sample.

Under these two headings may be included certain specialized
uses, *viz.*, determination of purity; differentiation of chemically

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*Superior numbers in the text refer to the bibliography at the end of
the chapter.

similar metals; analysis of glasses, refractories, etc., which are not amenable to chemical analysis; and analysis of electrodeposited films and biological tissues.   Spectrochemical analysis is also used as a guide and supplement to chemical analysis, as in the detection of interfering constituents and adsorbed impurities in weighed precipitates.

Owing to the ease, sensitivity, and rapidity of the spectroscopic method, it is now widely used in industrial analytical laboratories, either as the sole method of control or as a supplement to other methods.   Sawyer and Vincent[5] write that "the chemistry laboratory (Campbell, Wyant, and Cannon Foundry Co.) has entirely ceased to do any of the control analysis of the metallic constituents in cast iron," because the spectrograph permits qualitative and quantitative analysis of a sample for six minor constituents with a personnel time expenditure of less than one minute per determination.   "One man, single-handed, can post an analysis on a sample in seven minutes elapsed time." The quantitative accuracy is said to be better than 5 per cent. The same authors state that the analytical schedule of the Ford Motor Company exceeds 300 samples in a 16-hr. day and "the minimum time between the receipt of a sample and the posting of the analysis results is six minutes."

TABLE 1.—SYMBOLS AND UNITS

Quantity	Symbol	Units
Velocity of light...	c (cm./sec.)	2.998×10^{10} cm./sec.
Wave length......	λ (cm.)	Angstrom unit, A or Å. $= \dfrac{1}{6,438.4696}$ of the wave length of the Cd red line $= 10^{-8}$ cm. Millimicron, $m\mu = 10$ A $= 10^{-7}$ cm.
Wave number.....	$\nu' = \dfrac{1}{\lambda}$	Waves per centimeter
Frequency........	$\nu = \dfrac{c}{\lambda}$	Vibrations per second, Fresnel unit $= \nu \times 10^{-13}$

Probably the only legitimate disadvantage of the method is the fact that the interpretation of results is sometimes difficult. This is attributable in part to the excessive· sensitivity, which brings out every trace of impurity to confuse the analyst, but

in this the real fault lies more with the individual than with the method.

3. Units and Symbols.—Light will be considered as a sinusoidal transverse wave motion that travels at a velocity of 2.998×10^{10} cm./sec. in air, regardless of wave length or amplitude. Some of the terms employed to describe such waves are listed in Table 1.

The approximate wave lengths and frequencies of a portion of the electromagnetic spectrum are shown in Table 2 (page 27).

4. Types of Emission Spectra.—All spectra fall into one of two categories: emission spectra, which are produced directly by an excited source; and absorption spectra, which are due to absorption of light from a second source by the medium in question.
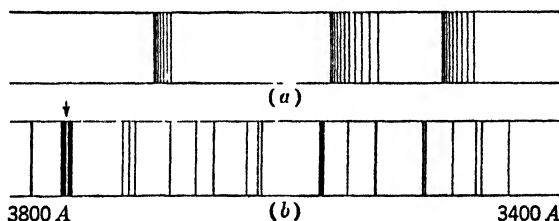
Fɪɢ. 1.—(*a*) Molecular spectrum; (*b*) atomic spectrum. (Note reversal of line marked by arrow. See Sec. 6.)

The following discussion is confined to emission spectra, which, in turn, may be classified according to their origin. The first type is produced, in general, by incandescent solids, certain types of electrical discharges, etc., and is characterized by the absence of *sharply defined* light or dark areas. Such a spectrum is called continuous. A second type is usually characterized by fluted bands or groups of lines which come closer together as they approach one end of the band called the head (Fig. 1*a*). These spectra are produced by suitably excited molecules and are therefore called molecular spectra. The third type of spectrum, which is of greatest importance in analytical chemistry, is characterized by sharply defined bright lines and is due to gaseous atoms or ions in a suitable state of excitation (Fig. 1*b*).

5. Origin of Atomic Spectra.—An adequate explanation of the physical theories concerning the production of spectra is beyond the intended scope of this book. The student should seek further information in texts by Thompson,[6] White,[7] Richtmyer,[8] Glasstone,[9] or any modern text on the theories of spectroscopy.

The following interpretation of the production of spectra should not be taken too literally but should be used merely as a working rule and basis for further study. Let us consider an atom to be a miniature solar system whose "sun" is a heavy, positively charged nucleus. The net charge of the nucleus is equal to the atomic number, *e.g.*, 1 for hydrogen, 2 for helium, 3 for lithium, etc. The electrons "revolving rapidly about the nucleus" are comparatively light and, owing to their negative charge, are attracted by the positive nucleus. The number of electrons that can be held by the nucleus equals the net charge of the nucleus, which in turn equals the atomic number. Thus the hydrogen nucleus can hold one electron, helium two, etc.

If an atom is in some way activated by thermal, radiant, or electrical energy, the various electrons may partially withdraw from the attracting nucleus and take up "orbits" at a greater distance. The potential energy of the atom is thereby increased because the electrons tend to return to their normal state. Since only certain orbits are possible, it follows that the atom may increase its energy content only by certain discrete values. Rather than talk about hypothetical orbits, physicists now refer to the various conditions of the electron as *energy levels*. Thus an atom whose normal energy state is represented by E_o may be excited to states of higher energy content as its electrons go to higher energy levels represented by $E_1, E_2, \cdots, E_n$.

Such an activated atom is then capable of losing part or all of its energy as each electron returns spontaneously to a lower energy level. The energy lost by the atom in this manner equals the difference between the energies of the initial and final energy levels; if an electron jumped from E_4 to E_3, the energy loss would be $E_4 - E_3$, etc. The energy lost by the atom because of these electron jumps is *radiated as radiant energy or light*. The frequency of this radiation varies directly with the amount of energy lost, as expressed by the basic equations

$$E_4 - E_3 = h\nu_a; \qquad E_3 - E_2 = h\nu_b; \qquad E_n - E_o = h\nu_n, \text{ etc.}$$

where h is a fundamental physical constant known as "Planck's constant of action" (6.55×10^{-27} erg sec.) and ν is the frequency. Note that the emission of energy must be discrete.

It so happens that not all the possible electron jumps or energy changes are permitted. For example, $E_7 - E_4$ and $E_6 - E_5$

may be possible changes but not $E_7 - E_5$. Also, the jump $E_7 - E_o$ may take place as such or in successive smaller jumps, $E_7 - E_6$, $E_6 - E_3$, $E_3 - E_o$. The many possible values of these energy changes are characteristic of the atom, and since each value corresponds to emitted light of a definite frequency, the observed distribution of these frequencies must also be characteristic of the atom. This grouping is, of course, the atomic spectrum.

It should be apparent that the number of observed spectral lines depends to some extent on the exciting energy of the source, since lines produced by large energy changes will not be possible unless the atom is sufficiently excited. Also, it is possible for the atom to be activated to such a state that an electron is removed completely. If this is the case, the atom will show a net positive charge, *i.e.*, it will become a positive ion owing to the removal of a negatively charged electron. The remaining electrons of this ion may be further excited to higher energy levels and in returning give rise to a new set of radiations characteristic of the ion. Note that atomic spectra may become less prominent under these conditions. This process may continue until several electrons have been removed, when the atom is said to be doubly, triply, or quadruply ionized. Very high exciting energy is necessary to effect such ionization, and spectra due to ions are observed for the most part in high-voltage spark discharges. Still higher excitation affects the tightly bound electrons nearer the nucleus and eventually gives rise to radiation in the X-ray region. Only the outer or valence electrons are in general responsible for visual and near ultraviolet radiation.

6. A measure of the ease with which atoms are excited to give their spectra is the energy required to raise an electron from its normal position to the next level. Another related measure of this quantity is the energy required to remove the electron from the atom altogether. The energy may be measured electrically and expressed as the *resonance potential* for the first case and as the *ionization potential* in the second case (Fig. 2). Note that these energies might be calculated from the basic equation $\Delta E = h\nu$ and that the resonance potential represents the energy required to excite the atom to just emit one frequency corresponding to $E_1 - E_o$ where E_1 is the lowest excited state and E_o is the normal state. The ionization potential, on the other hand,

represents the energy required to cause the atom to emit all the lines of its spectrum, since any greater excitation produces lines characteristic of the ion.

Note that the electronic configuration of an ionized atom is similar to the electronic configuration of an un-ionized atom one number lower in the periodic table and that therefore the two
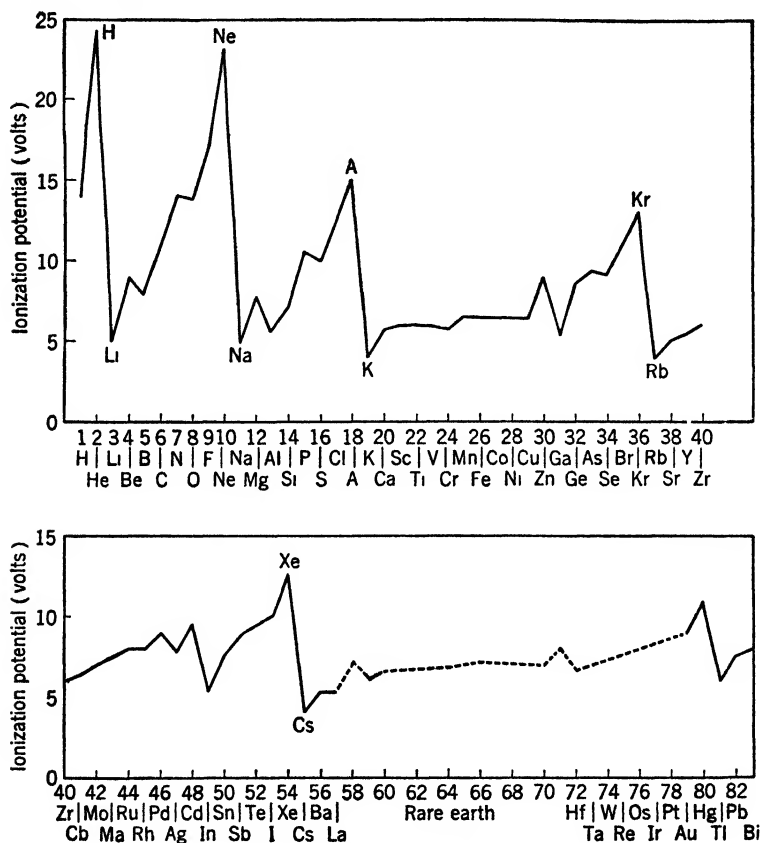
Fig. 2.—Ionization potentials of the elements.

spectra should be somewhat analogous, as indeed they are [K and Ca(I), etc.].   Another important point brought out by the foregoing theory is that the intensity of a spectral line does not depend so much on the exciting energy of the source as on the tendency of the atom to show the one particular energy change responsible for the line.   The exciting energy must be sufficient,

of course, to excite the atom to the requisite energy level. Further, if the atom is exposed to sources of sufficient energy, the lines of the atomic spectrum may actually become fainter owing to the predominating ionic form.

An additional factor that affects the intensity of some of the stronger spectral lines is the tendency to "reverse." This phenomenon is usually manifested by the appearance of a dark area down the middle of the emitted line which may almost entirely blot out the latter. The reversal is due to absorption occurring in the relatively cooler atomic vapors surrounding the source and may be demonstrated experimentally by passing monochromatic light from a sodium arc through a layer of sodium vapor. After passing through the vapor, the D lines will be partially reversed because of absorption. The reason for this change becomes clear if we remember that the atoms of sodium in the vapor may absorb radiant energy and store it as potential energy by moving an electron to a higher level. The energy so absorbed will be given by the expression $E_a = h\nu_a$ which is identical with the expression $E_e = h\nu_e$ for the light energy emitted by an excited atom. If the same electron is involved in absorption as in emission, then $E_e = E_a$ whence $\nu_e = \nu_a$. Thus the emission mechanism may be considered as reversible, the expression $E = h\nu$ being applicable in either case. Observe that in order to absorb light effectively, the atom must be relatively stable in its excited condition.

METHODS OF EXCITATION

7. Excitation by Flame.—The low-temperature flame of the Bunsen or Meker burner suffices for the excitation of a few lines of the spectra of the alkali metals and some of the alkali-earth metals. The metals should be in the form of their chlorides in most cases, since these salts are relatively volatile. A conventional procedure is to introduce the sample into the flame by means of a wick made from a bundle of fine platinum wires or from asbestos fibers sealed in the bottom of a short Pyrex tube (Mitscherlich tube). Another method consists of soaking pumice or porous graphite in the solution and then heating in the flame. A large excess of ammonium acetate is sometimes added to the solution.

For serious work, the method of Lundegardh[17,21,22] is employed. A suitably prepared solution of the sample is placed in an atomizer

(Fig. 3) connected to the air inlet of an air-acetylene or oxyacetylene torch.   The flame provides a steady source for spectroscopic or spectrographic study, and the exciting energy is considerably higher than that of the Bunsen flame, although not so high as the arc source discussed below.   Lundegardh claims that 32 elements may be determined by this method, *viz.*, Ag, Au, Ba, Ca, Cd, Co, Cr, Cs, Cu, Dy, Fe, Ga, Gd, Hg, In, K, La, Li, Mg, Mn, Na, Nd, Pr, Nl, Pd, Rb, Rh, Ru, Sr, Tl, Y, Zn (and also Cl, Br, I, SO_4 in some cases).   The spectra are relatively poor in lines, but this is not particularly disadvantageous.   The spectral background is
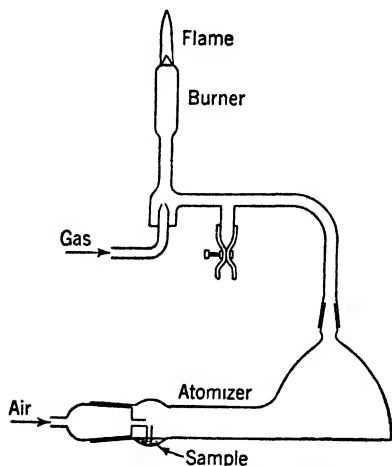
FIG. 3.—Lundegardh apparatus.

not heavy and consists for the most part of molecular bands due to water vapor.   Ramage[23] employs an oxyacetylene flame into which a moist filter paper containing the desired substance is slowly introduced.

8. Excitation by the Electric Arc.—This method is probably the most widely used and the most satisfactory of the three methods commonly employed for analytical spectroscopy. The arc is simple to operate, requires little equipment, shows a spectrum of many lines, most of them due to neutral atoms, and is considered to be the most sensitive source, *i.e.*, it excites lines of metals present in exceedingly minute amounts.   Its principle advantage over the spark method, which will be discussed later, is this high sensitivity and the fact that arc spectra are sometimes more representative of the sample than spark spectra, which may be unduly selective.   For quantitative work of some types, the arc is especially suitable, since it permits complete burning of the sample.   The principal disadvantage is its instability, or tendency to flicker and wander, which results in a somewhat lower degree of reproducibility, although this difficulty may be overcome to a large extent by the 2,000-volt a.c. arc described later on.

The electrical circuit for the arc is shown in Fig. 4.   Voltages of 50 to 250 volts d.c. may be used, the higher voltage being pre-

ferred because it gives a steadier arc.   Steadiness is likewise
increased by the reactance, which is simply a coil of heavy wire on
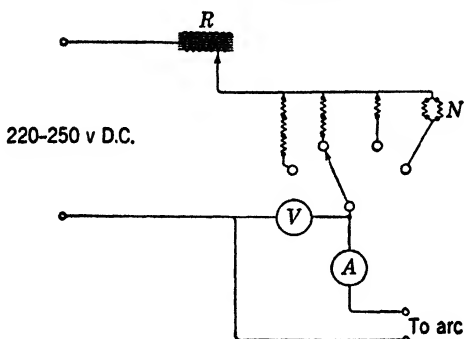
FIG. 4.—Wiring diagram for arc source.
R = reactance
N = high-capacity variable resistance (20-ohm heating coils)
V = voltmeter
A = ammeter

an iron core.   Although excessive reactance reduces the sensitiv-
ity of the arc somewhat, the general rule is to use as large a react-
ance as possible.   The reason is apparent from the fact that the
voltage and amperage of an un-
ballasted arc may vary by as
much as 50 per cent as the arc
wanders.[24]   The pulsating direct
current of a half-wave rectifier is
suitable for arc excitation and is
even said to give increased
sensitivity.[25]

The electrodes of the arc are
supported by an insulated arc
stand which permits delicate ad-
justment of each electrode (Fig.
5).   The lower electrode is some-
times constructed so that it is
capable of rotation by a small
motor.   Rotating the lower elec-
trode at about 600 r.p.m. steadies

FIG. 5.—Arc or spark stand.
(*Courtesy of Central Scientific Com-
pany.*)

the arc considerably.   To facilitate focusing the arc gap on the
slit of the spectroscope, the correct position of the gap may be
indicated by a rigid pointer attached to the stand.

The electrodes themselves may be of carbon, graphite, or some metal such as copper or silver.   Carbon electrodes give a steadier arc than graphite, but the latter is more generally used because of its purity and high conductivity.   Graphite electrodes may be purchased either in a very pure state ready for use or in less expensive crude form (Acheson).   It is common practice to buy the latter in $\frac{1}{4}$- and $\frac{3}{16}$-in. diameters and process them.   The $\frac{3}{16}$-in. rods are cut in $1\frac{1}{2}$-in. lengths, and one end is drilled with a clean, greaseless twist drill to a depth of a few millimeters.   The hole should be as large as possible without giving rise to undue breakage of the wall.   Myers and Brunstetter[26] give directions for drilling the electrodes with a special lathe tool.   A convenient motor-driven device is now on the market (Jarrell-Ash Co.) After drilling, the outer edges of the electrode should be beveled slightly with a clean file.   Otherwise the arc may wander about the sharp rim.   The $\frac{1}{4}$-in. rods are cut in 2-in. lengths and sharpened in a pencil sharpener or with a clean file.   Alternatively, the ends may be ground flat and a shallow depression bored in the center.   The purpose in either case is to steady the arc.

After shaping, the electrodes may be used at once, if purity is not essential, or they may be purified by one of several alternative methods.   The impurities that are apt to be present include Cu, Ag, Sr, Ba, Be, Cr, V, Ca, Fe, Mg, Ti, Zn, Pb, and also B and Si, but none of these is generally present in sufficient quantity to give more than a few very faint lines.[27]   For most purposes, a simple partial purification is sufficient.   The easiest procedure is to heat each electrode to 2500°C. in a vacuum oven.[28]   If such an oven is not available, the extraction procedure of Staud and Ruehle[29] is used.   The electrodes are first heated to bright redness in a silica dish, then cooled and refluxed for 24 hr. in vacuum-distilled 1:1 sulfuric acid.   They are then washed, refluxed, and washed again until acid free.   (A large Soxhlet extractor is recommended.) The final step is heating to bright redness in an oxy-gas flame.   A preliminary arcing at 10 amp. for 1 min. removes most of the residual impurities which include traces of B, Si, Ca, and Ti, and sometimes Fe.   If these are to be completely removed, the lengthy procedure of Standen and Kovach[30] is advisable.

Metallic electrodes are best purchased from a dealer in spectroscopic equipment.   Their principal advantages are that they

provide a reference spectrum superposed on the spectrum of the sample and that the continuous background of the carbon or graphite arc is eliminated.   The latter is especially objectionable in the violet and near ultraviolet region where the intense band spectrum of cyanogen is located.   In addition, metallic electrodes are better thermal conductors and thus prevent too rapid volatilization of the sample.   Lewis[31] recommends general use of copper electrodes, especially for quantitative work.   (For a discussion, see Brownsdon and van Someren.[32])   Iron electrodes are used for the study of ferrous materials which sometimes fail to give a good spectrum when supported by graphite.

The general procedure for transferring the sample to the crater is to employ a sleeve of glass tubing which fits tightly around the electrode.   The sample is introduced through a small funnel whose stem is placed in the projecting part of the sleeve.[33] Samples of 1.0 to 50 mg. are usually used.   An alternative method recommended by Lewis[31] is to compress the sample into a small pellet which is then placed in the crater.   In either method, the electrode is weighed alone and again after addition of the sample.

If solutions are to be analyzed, the electrode is usually of larger diameter and has a crater holding about 0.2 ml.   If the electrode is of carbon or graphite, it is usually dipped in redistilled kerosene in order to make it waterproof.   A film of collodion is also used for the same purpose.   About 0.1 ml. of the concentrated solution of sample plus base mixture (Sec. 11) is then evaporated in the crater at 105 to 110°C.   If it is desired to concentrate a particular metal from a solution, the electroplating procedure of Bayle and Amy[34] may be tried.

The arc is struck either by bringing the two electrodes together and separating, or by brushing the gap with a graphite rod provided with an insulating handle.   The arc is focused on the slit, rapidly adjusted to 4 or 5 mm., and the exposure is commenced.   It is advisable to watch the burning with a hand spectroscope so that the beginning and end may be noted and the exposure controlled accordingly.   In some cases, it is advisable to stop the arc after a few moments and break away the walls of the crater so as to expose the fused globule of sample.   It is also good practice to start the arc at low amperage and then increase it as the volatile constituents become exhausted.   For most work, it is best to make the lower electrode the anode ($+$), since

it is hotter.   In the case of metallic samples which melt to form a globule in the crater of the graphite support, the polarity should be adjusted so that the arc strikes to the globule and is steady. This is usually the case when the globule is the anode.

Attention should be called at this point to several modifications of the arc method: The steadiness of the arc may be improved by rotating the lower electrode, as mentioned above, and, further, by using a hollow upper electrode through which a current of air is sucked.   This not only steadies the arc but aids in volatilizing the sample.   Extremely rapid volatilization of the sample is accomplished in the method of Hasler,[35] who uses an annular hollow anode filled with the sample and a volatile carrier such as ammonium chloride.   General information on the arc source is given by Baly,[36] Vincent and Sawyer,[5] Chaney, Hamister, and Glass,[38] and Hasler.[39]

The potential gradient between various points in the arc itself is highest near the negative pole.   The cathode region, therefore, gives somewhat higher excitation than the rest of the arc.   This fact is utilized in the "Glimmschicht," or cathode-layer method developed by Mannkopff and Peters.   The procedure is outlined in a book by Strock[37] and consists essentially of reversing the polarity of the arc so that the lower, drilled electrode is the cathode, and focusing the image of the cathode region of the arc on the slit of the spectrograph (see Fig. 19e).   A 220-volt 10-amp. current is employed.   This method of excitation requires only 2 or 3 mg. of sample and gives somewhat higher sensitivity, but the necessity of focusing a 1- or 2-mm. portion of the arc on the slit is somewhat disadvantageous because of the tendency to wander.   The method is widely used, however, and is indicated whenever high sensitivity is desired.

The Pfeilsticker[42] arc, which combines the advantages of arc and spark, is simply a 220-volt a.c. arc which is excited at the peak of each cycle by a timed spark discharge produced by a Tesla coil. An interrupted arc which involves a make-and-break device such that the arc electrodes are brought together and separated several times a second is discussed by Gerlach and Gerlach.[27]

The high-voltage a.c. arc of Duffendack and Wolfe[40,41] possesses all the advantages and characteristics of the low-voltage arc and is a much steadier and more reproducible source for quantitative work.   A simple circuit suitable for exciting such an arc is shown

in Fig. 6. The transformer is of the type commonly used in municipal lighting systems as a pole transformer, and the variable resistance may be of the simple type described above, *i.e.*, constructed from 500-watt heater units in series. The entire arc assembly should be surrounded by a cage or metal box to protect the operator from the dangerously high voltages employed. Duffendack and Wolfe recommend $\frac{1}{2}$-in. lengths of graphite rods as electrodes. These are cut flat, smoothed, and slightly rounded to eliminate sharp edges. The sample, in the form of a solution, is evaporated on the tips of the electrodes which are then dried and placed in a special arc stand equipped with a very fine adjusting mechanism. The arc is started by approaching the two electrodes and then withdrawing to a gap of $\frac{1}{2}$ to $1\frac{1}{2}$ mm. The
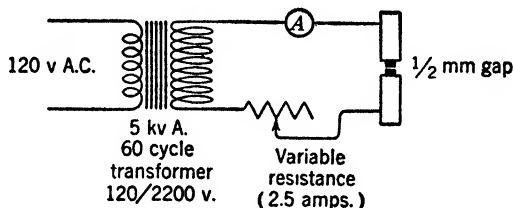
Fig. 6.—High-voltage a.c. arc circuit.

separation of the electrodes, the voltage, and the amperage should be carefully controlled in order to obtain the reproducibility of results for which this source is principally noted.

9. Excitation of Spectra in a Spark Discharge.—Four types of spark excitation are used in practice, each possessing some slight advantage over the others. A review of the inherent problems is given by Kaiser.[43]

The advantages of the spark over the arc methods of excitation are not so well defined as might be expected from the differences in exciting energy. The spark excites predominantly ionic spectra, which are usually no more sensitive than the atomic spectra, but the high exciting energy brings out the lines of certain nonmetals such as C, Si, P, B, and Te more strongly than does the arc. Other advantages such as reproducibility and stability are of critical importance only in quantitative work. The greatest two advantages of the spark are: its ready applicability to the analysis of solutions and the fact that less material is required. The four methods will be treated in the following paragraphs.

The condensed spark,[44] which is probably more generally used than other spark methods, is produced by a transformer or induction-coil circuit arranged as in Fig. 7. The purpose of the inductance I, which is simply a coil of wire wound on an insulating tube, is to suppress emission of spectral bands due to air. Too large an inductance, however, leads to reduction in sensitivity and overheating of the electrodes. If an induction coil is used,
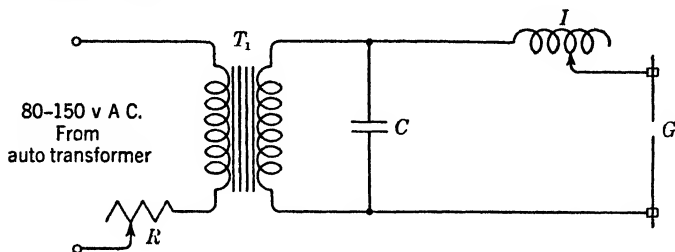
Fig. 7.- Condensed spark circuit
R resistance
T_1 = transformer, 0 25 kw. 120/15,000 volts
C = condenser 0.006 mf
I = air-core inductance 30 to 1,000 μh.
G = gap
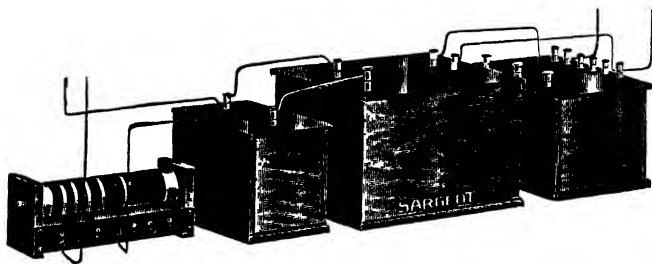
Fig. 8.—Equipment for condensed spark. (*Courtesy of E. H. Sargent & Company.*)

it should be capable of a 4- or 5-in. spark. Baly[36] gives directions for constructing the necessary inductance, condenser, etc.

The condensed-spark method for examination of solids consists of fusing the solid with sodium carbonate in a shallow platinum dish which is one electrode of the spark. The mixture is kept fused by means of a Bunsen burner, and a spark from an upper pointed electrode of gold or platinum is allowed to impinge on it. This method is not particularly satisfactory and is replaced, whenever possible, by a method involving solutions. It is sometimes possible to analyze solid samples by placing them in the crater of a graphite electrode; but more commonly the sample is dissolved, mixed with a filler, and evaporated

either on the polished, oiled surface of the electrode, in a waterproof crater, or in the pores of a piece of graphite that has been arced for a few seconds.

A more satisfactory means of dealing with solutions is the use of a cell similar to that described by Twyman and Hitchen,[44] as shown in Fig. 9. The solution of sample, which must be rendered conducting by the addition of about 5 per cent HCl, is allowed to flow from the reservoir A up to the jet D, which is made of Pyrex or clear silica. As the solution flows through the jet, a spark is passed from the upper carbon or metal electrode F. The shield B protects the operator from spatterings. The opening E, sometimes covered by a thin plate of quartz, permits passage of light to the spectrograph.

The Feussner[45] *spark* may be used in the same way and is simply a condensed discharge that takes place only when the condenser is at its peak voltage (Fig. 10).

The uncondensed spark[27] is produced directly by the secondary of a heavy induction coil or transformer without condenser or reactance. Greater sensitivity is claimed, but the strong background is usually objectionable. The method may be used for sparking solids which are mounted in a short iron tube. The great heating effect of the spark keeps most materials fused. Solutions may be analyzed in a shallow platinum dish-shaped

FIG. 9.—Sparking device for liquids (Hitchen type).

A = reservoir
B = glass jacket and splash guard
C = glass or Duprene seal
D = silica or Pyrex jet (detailed inset)
E = quartz window
F = carbon electrode or gold-wire electrode
G = gold wire
H = copper wire
I = rubber tubing

electrode cooled from below with ice and water (Fig. 11), or the above-mentioned technique employing graphite electrodes may be used.

The high-frequency spark, developed by Gerlach and Gerlach,[27] presents the outstanding advantages that it may be used for the analysis of thin films, *e.g.,* electroplated layers or moist filter
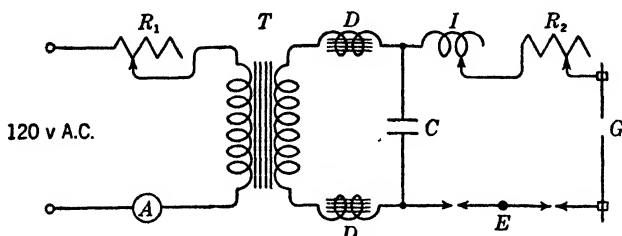
FIG. 10.—Feussner or controlled-spark circuit.   [*See Ann. Physik,* **34,** 297 (1939).]

R_1R_2 = variable resistors
T = 120/12,000-volt transformer
DD = choke coils
C = condenser
I = inductance
G = spark gap
E = synchronized interrupter
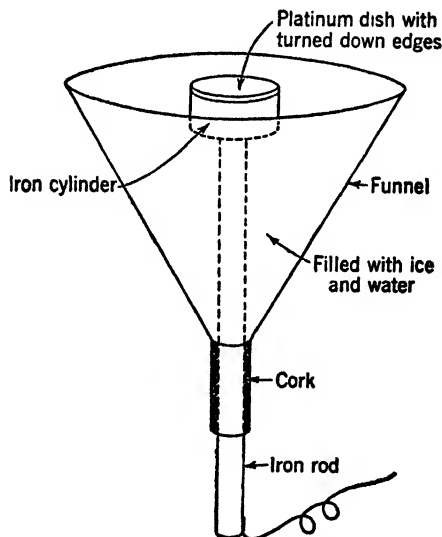
FIG. 11.—Cooled electrode used for uncondensed spark.   (The meniscus of the solution in the platinum dish should be slightly above the level of the edge of the funnel.)

papers, and also for the analysis of untreated biological tissues, etc.   It is exceedingly sensitive, and the elimination of the need for preparing the sample makes for less contamination.   Owing

to the very high frequency, the discharge penetrates nonconducting materials. The setup is shown in Figs. 12, 13, and 14.

In practice, the sample is placed on a piece of filter paper F (3 by 4 cm.) which rests on a clean glass plate P (9 by 12 by 0.05 cm.). The support is a plate of aluminum mounted on a ball-
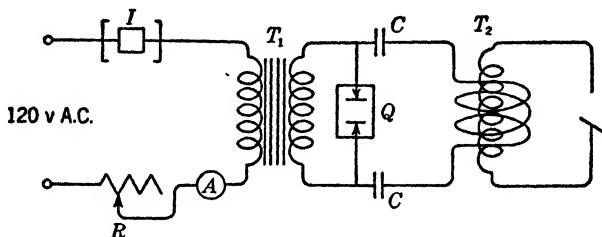
FIG. 12.—The high-frequency spark circuit.

I = interrupter (used only if T_1 is an induction coil)
T_1 = transformer 120/12,000 volts, 0.8 kw., or induction coil
CC = condensers 0.004 mf.
Q = quenched-spark gap, enclosed
T_2 = Tesla coil: primary—16 turns 2-mm. copper wire; secondary—140 turns 1.2-mm. copper wire
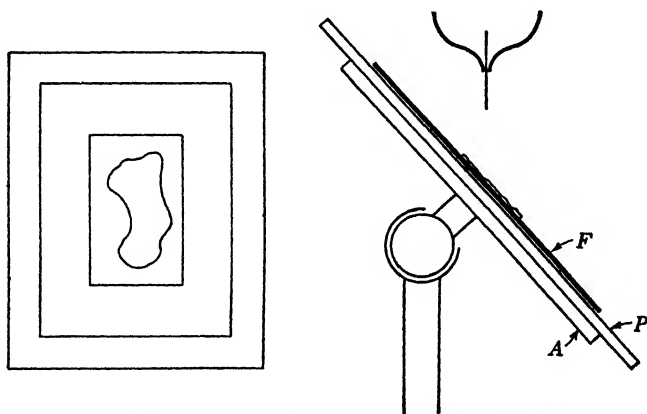
FIG. 13.—High-frequency spark electrodes for biological work.

and-socket joint (Fig. 13). The sample and filter are continuously moistened with 10 per cent aqueous $NaNO_3$ to prevent flame as the spark is passed from a 0.2- to 0.5-mm. gold or platinum wire (Fig. 14). The sample is moved about until entirely consumed. The emission spectrum resembles that of an arc rather than a spark, the spark lines being suppressed to a considerable degree.

10. Other Methods of Excitation.—Several modifications of the preceding methods have been developed to fill immediate needs. Hultgren[46] uses a "spark in flame" method whereby a Lundegardh flame is directed between spark electrodes. Underliquid arcs have been used,[17] and a liquid sample may be sprayed into a spark by the procedure of Lamb.[47] Keirs and Englis[18] employ a hollow upper electrode of carbon through which a solution is allowed to flow during a spark discharge. One of the most popular modifications is that of Scith and Hofer:[114] a powerful jet of air is directed at the spark to remove the envelope of cool

Copper

Glass tube

Mica

Picein

Platinum
or gold wire
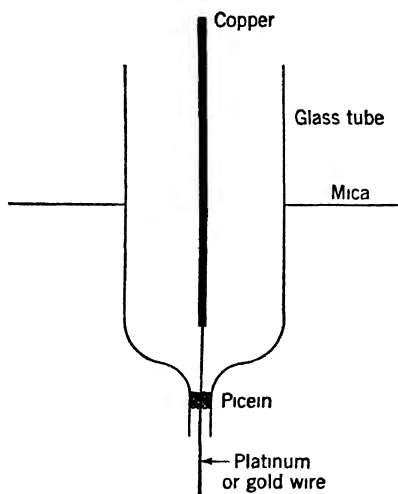
Fig 14   Upper electrode of Fig 13.

un-ionized vapor which causes absorption and reversal. This method is widely used for quantitative analysis of metals.

11. Preparation of the Sample.—Unless the sample is received in the form of a metallic rod or wire, it is usually desirable to modify it in such a way that the emission of a brilliant and representative spectrum is facilitated. The method of preparing the sample depends on its nature as well as on the method of excitation employed. The method of preparation of samples for qualitative spectrochemical analysis may differ slightly from that used in preparing samples for quantitative work (Sec. 31).

Although it is difficult to lay down procedures that apply to every case, the following rules may well serve as a general guide:

Metals.—Metals in bulk form may be used directly as electrodes for an arc or spark discharge. If only one piece of metal is available, it may be used as the cathode of an arc whose anode is of carbon or graphite. Samples of fine wire may be used as spark electrodes or may be fed into the anode crater of a carbon arc. Filings are either fused in the crater of an arc or dissolved in aqua regia or other acid and treated as solutions. Excess acid should be fumed off.

Easily Volatile Inorganic Solids.—Salts, oxides, etc., are ground to a fine powder and mixed intimately with an equal quantity of powdered graphite. The mixture may be tamped into the prepared crater of a graphite electrode or first compressed in a pellet press. If desirable, a dry flux may be mixed into the powder prior to arcing, in order to fix the mass in the form of a molten globule. The nature of the flux is governed by the chemical nature of the specimen to some extent. Sodium nitrate, sodium chloride, sodium carbonate, calcium carbonate, silica, or mixtures of sodium chloride and silica are commonly used. For quantitative work, Brode[10] recommends a flux consisting of 100 parts alumina (Al_2O_3) plus 25 parts hydrated silica (H_2SiO_3).

The volatility of certain halides is sometimes undesirable, especially if other nonvolatile materials are also present. Fuming the sample to dryness with sulfuric acid converts these halides to the less volatile sulfates. A silica dish or crucible is recommended for this operation.

Nonvolatile Inorganic Solids.—Ceramics, glasses, slags, etc., are powdered and mixed with graphite powder to render them conducting and either arced as such or with a volatile assistant such as ammonium chloride or sulfate. The ammonium salt volatilizes rapidly and in so doing helps to transport the fused particles of the sample into the arc. Sodium and calcium carbonates are sometimes used for the same purpose.

Organic Solids or Mixtures Containing Organic Matter.—Such specimens are subjected to a wet-ashing procedure prior to excitation, except those which are amenable to excitation by the high-frequency spark method. In the usual procedure, the sample is charred with sulfuric acid, and nitric acid is added dropwise to the boiling mixture until it becomes colorless. The solution is heated to fuming and then either diluted and used directly in a sparking tube or fumed to dryness and treated as above.

Dry ashing at 300 to 400°C. is also possible as an alternative to the wet method, but is not generally so rapid.

Solutions of Inorganic Material.—Solutions are most conveniently used as such in a Hitchen sparking tube. A small amount of an electrolyte such as HCl is added to increase the conductivity. Solutions may likewise be evaporated in the prepared crater of a graphite electrode which is then made the anode of a d.c. arc. A flux or assistant may be added if necessary. For quantitative work, the solution may be evaporated in the porous tip of a graphite rod, or in a shallow crater that has been waterproofed, and the rod used as one pole of a high-voltage a.c. arc. If spark excitation is employed, the solution is evaporated on the flat oiled tip of a graphite rod. Unless otherwise stated, it is assumed that whenever a liquid is evaporated on graphite or carbon the latter has first been waterproofed by dipping in distilled kerosene or in a dilute collodion solution. Solutions may also be excited by spraying into the Lundegardh flame, or by absorption on a filter paper which is then held in the flame. Also, a solution may be added to the above-mentioned alumina-silica flux, which is then stirred to a thick paste and dried by heat. The solid is ground and placed in the crater of an arc. This procedure is recommended for quantitative work where a d.c. arc must be used.

Attention should be called to the advisability of concentrating extremely dilute solutions prior to spectrochemical analysis. This step, which is all too often neglected by spectroscopists, enhances the sensitivity many times. The use of organic precipitants in conjunction with spectrochemical analysis presents interesting possibilities (see Hibbard[12]). Electrolytic preliminary separation is an accepted procedure for lead analysis and has been used to some extent for other metals.[13] Coprecipitation of the desired substance together with a bulky precipitate of a similar nature is a favorite technique.

Although the foregoing rules may serve as a general guide, it is well to refer to the literature for specific methods that have proved eminently successful for certain types of specimen. Such data are readily available in the large number of publications on spectrochemical analysis. See especially Rohner;[14] Ruehle and Jaycox;[15,18] Hess, Owens, and Reinhardt;[16] Lundegardh;[17] Ewing, Wilson, and Hibbard;[19] and Nitchie.[20]

12. Whenever chemicals are added to a sample, it is necessary to make a spectrographic analysis of the added chemicals in order to demonstrate their purity, or at least the absence of constituents which may be present in the sample. All chemicals should be "superpure." Sulfuric acid must be redistilled under vacuum, and all other liquids must be redistilled in a Pyrex or silica still. Ammonium sulfate is easily made by passing gaseous ammonia into distilled sulfuric acid. Other chemicals, which cannot be prepared from distilled materials, are purified by repeated recrystallizations. Reagents are kept in Pyrex or silica bottles to avoid contamination from lead and other metals present in ordinary glass. The so-called Specpure powders or superpure salts, sold by A. Hilger, are exceedingly useful as comparison standards or bases.

SPECTROSCOPES AND SPECTROGRAPHS

13. A spectroscope is an instrument designed for visual observation of spectra. The term is also used in a more general
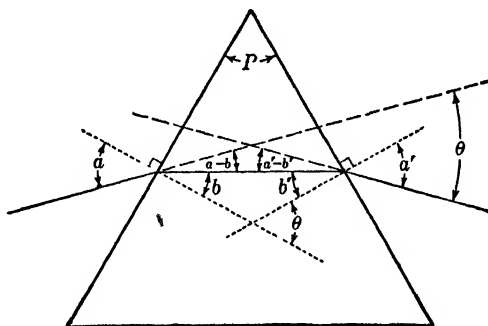
FIG. 15.—Deviation in a prism.
θ = deviation
P = prism angle

sense to describe any instrument producing a spectrum. A spectrometer is a spectroscope equipped with a scale for measuring wave lengths. A spectrograph is a modified spectroscope designed for photographic recording of spectra and is used almost exclusively in serious work because of its rapidity and the fact that it yields a permanent record.

Light may be dispersed by either of two methods: by refraction, as in a prism, or by diffraction, as by a ruled grating. The following sections will be given over to brief descriptions of some

of the more common spectroscopic instruments employing these two principles, with a preliminary discussion of the theory involved.

14. Prismatic Dispersion.—The passage of light through a prism is shown in Fig. 15, where P is the apex angle of the prism. It may be shown[36] that when θ is at a minimum, then

$$(I) \qquad n_{\text{prism}} = \frac{\sin a}{\sin b} = \frac{\sin a'}{\sin b'} = \frac{\sin\left(\dfrac{\theta + P}{2}\right)}{\sin\left(\dfrac{P}{2}\right)}$$

The variation of the refractive index of any substance with wave length may be expressed as

$$(II) \qquad n = n_o + \frac{c}{(\lambda - \lambda_o)^a}$$

where n_o, λ_o, a, and c are constants. If a is approximately equal to 1, then

$$(III) \qquad \frac{\delta n}{\delta \lambda} \cong - \frac{c}{(\lambda - \lambda_o)^2}$$

Further, on differentiating (I),

$$(IV) \qquad \frac{\delta\theta}{\delta n} = \frac{2\sin\left(\dfrac{P}{2}\right)}{\cos\left(\dfrac{\theta + P}{2}\right)} \qquad \text{(radians)}$$

But since

$$a = \frac{\theta + P}{2}$$

then

$$(V) \qquad \frac{\delta\theta}{\delta n} = \frac{2\sin\left(\dfrac{P}{2}\right)}{\cos a} = \frac{2\sin\left(\dfrac{P}{2}\right)}{\sqrt{1 - \sin^2 a}}$$

but $\sin a = n \sin b = n \sin (P/2)$ from (I); hence

$$(VI) \qquad \frac{\delta\theta}{\delta n} = \frac{2\sin\left(\dfrac{P}{2}\right)}{\sqrt{1 - n^2 \sin^2\left(\dfrac{P}{2}\right)}}$$

and if $P = 60°$, $\sin P/2 = 0.500$ and

(VII)
$$\frac{\delta\theta}{\delta n} = \frac{1}{\sqrt{1 - \dfrac{n^2}{4}}}$$

but $\dfrac{\delta\theta}{\delta n} \cdot \dfrac{\delta n}{\delta\lambda} = \dfrac{d\theta}{d\lambda} = D$, which is the desired dispersion.

(VIII)
$$D = \frac{d\theta}{d\lambda} = \frac{1}{\sqrt{1 - \dfrac{n^2}{4}}} \cdot \frac{c}{(\lambda - \lambda_0)^2}$$

where θ is in radians; 1 radian $= 57.3°$.

The constants n, c, and λ_0 of this equation may be calculated from experimental observations, and $d\theta/d\lambda$ may be computed for any desired wave length. It follows that as the latter becomes smaller (toward the ultraviolet) the dispersion D increases.

An alternative method of evaluating dispersion is to plot a curve of the linear dispersion, i.e., angstroms per millimeter, vs. wave length. The linear dispersion is a more convenient value for spectrographic use

Fig. 16.—Dispersion—deviation curve for a typical prism spectrometer.

where a picture of the spectrum (spectrogram) is measured with a ruler to determine wave length. A typical dispersion curve is given in Fig. 16.

15. A closely related quantity called the *resolving power* indicates the ability of a given spectroscope to resolve two spectral lines separated by the distance $d\lambda$. This ability will obviously depend to some extent on the dispersion, which in turn depends on the wave length. The quantity $\lambda/d\lambda$ is commonly used as the measure of resolving power R. It may be shown[36] that the maximum value of R is given by

$$R = \frac{\lambda}{d\lambda} = r\frac{d\theta}{d\lambda} = t\frac{\delta n}{\delta\lambda}$$

where r is a constant and t is the thickness of the base of the prism. The value of R is affected, however, by the width and shape of the slit and by the characteristics of the optical system.

The narrower the slit, the better the resolving power up to a certain point, but the less the illumination. A compromise between these factors gives an optimum slit width of several times the theoretical slit width $f\lambda/4d$, where f is the focal length of the collimating lens, λ is the wave length, and d is the diameter of the collimating lens, all in millimeters. The optimum slit width is best determined experimentally as described in Sec. 16. The quantity f/d is a measure of the light-gathering power of a spectroscope and is called the *aperture ratio*. The smaller the aperture ratio, the brighter the spectrum, other factors being
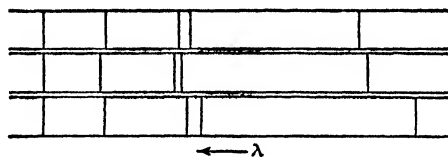
Fig. 17.—Irrationality of dispersion. Spectra of the same source produced by three geometrically identical prisms of different materials.

equal. The optical theory involved was worked out by Schuster[49] (see also the work of Stockbarger and Burns[51]).

Resolving power is usually determined by observing pairs of lines in a known spectrum and noting whether or not certain doublets are resolved. An instrument that just resolves the sodium doublet $5{,}890 - 5{,}896$ A will have a resolving power of $5{,}893/6 = 982$.

16. The Simple Prism Spectroscope.—The essential features of this familiar instrument are shown in Fig. 18. The function of lens L_1 is to concentrate light from the source (not shown) into an image on the slit S. The slit then acts as a narrow brilliant aperture from which rays proceed to fill the collimator L_2, which renders them parallel for passage through the prism P. The refracted rays are focused by the telescope lens L_3 in the plane of the cross hairs X. By moving the telescope arm T, a ray of any desired wave length is brought to the cross hair and the slit image or spectral line is examined through the magnifying eyepiece E. The size of the lines observed is a function of the size of the slit and the magnification of the system.

To adjust the spectroscope, the eyepiece is focused on the cross hairs and the telescope is focused on infinity by observing the reflection of a distant source in the side of the prism. If the focus is correct, no parallax will be observed between the focused image and the cross hairs. The collimator is then focused by observing the spectrum of the sodium flame and moving the tube carrying the slit until a sharp line is seen through the eyepiece. The center of the slit should coincide with the cross hairs. Further adjustment of the instrument may be made in accordance with directions furnished by the manufacturer (see also Reilly and Rae[50]).
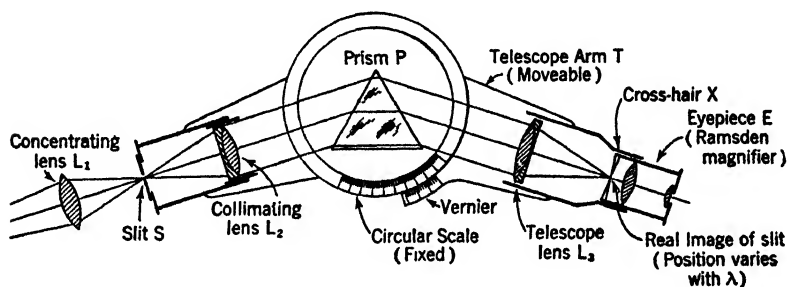
FIG. 18.—The simple spectroscope (spectrometer).

The slit should be cleaned, if necessary, with a splinter of soft wood and closed to a suitable setting (see Sec. 15). An approximate value for the optimum slit width is obtained by closing the slit until a sharp spectral line ceases to become narrower and merely becomes less brilliant. Great care should be taken never to close the slit entirely, for the jaws may be seriously damaged. The slit opening must be parallel to the edge of the prism, *i.e.*, the image at the cross hairs must be vertical.

Adjustment of the source and condensing lens L is accomplished as follows: First place the source some distance from the slit and see that it is aligned with the collimator. Then place the condenser in such a position that the focused image of the source on the slit completely covers the latter. The condensing lens should be optically good and have a focal length in the vicinity of 25 cm. (see Fig. 19).

Stockbarger and Burns[51] give an excellent discussion of the various methods of slit illumination and their relation to resolving power. It is found that the most brilliant spectra are obtained

when the collimator is filled with light (Fig. 19b), but that the resolving power is at a maximum when the condenser is stopped down so that the collimator aperture is only about half-filled with light.   Ballard and Gow[52] describe a rectangular diaphragm for reducing the aperture of the condenser in order to cut down
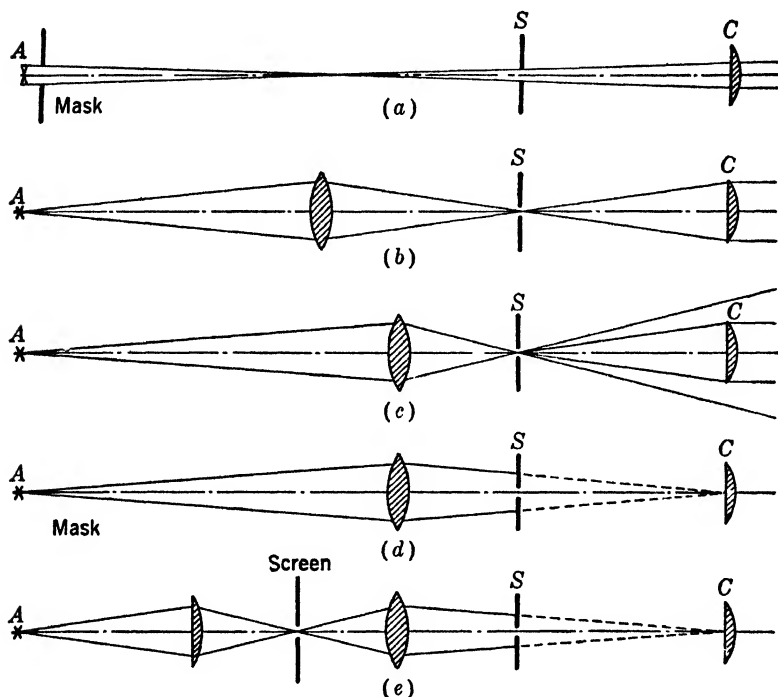
Fig. 19.—Illumination of the slit. A = source; S = slit; C = collimator.
(a) Without condenser— low intensity, ends of electrodes must be masked. (b) With condenser—maximum intensity but slit may not be uniformly illuminated by image of source.   (c) Incorrect use of condenser—light is wasted.   (d) Condenser focused on collimator—low intensity, but slit uniformly illumined. In practice, the condenser is placed nearer the slit, and for quantitative work, (Sec. 34) the sector disk is placed immediately in front of the slit.   (e) Arrangement of Twyman and Simeon—gives intense and uniform illumination and permits isolation of particular areas from source.

the illumination.   The most versatile method of illumination is that described by Twyman and Simeon.[80]   This arrangement (Fig. 19e) is used for quantitative analyses where uniform illumination is particularly necessary.

To measure wave lengths, it is necessary to calibrate the scale by noting the readings for known spectral lines (Table 2).   If the

instrument reads in degrees, a curve of degrees vs. wave length may be constructed, or if the instrument reads wave length directly, a scale-error graph should be plotted.

17. Other Prism Spectroscopes.—The simple instrument described above is seldom used as such because of the low disper-

TABLE 2.—RELATION OF COLOR, WAVE LENGTH, FREQUENCY, AND WAVE
NUMBER

Important spectral lines ($m\mu$)	λ Wave length ($m\mu$)	ν Frequency (fresnel)	ν' Wave number (cm^{-1})
	Color		
	---- 750 ------------- 400 ------------- 13,340		
	Red		
Li 670 8			
H(c) 656 3			
	---- 620 ---- Orange ---- 484 ------------- 16,140		
Na(D) 589 6}	---- 600 ---- Yellow ---- 500 ------------- 16,670		
589 0}	---- 580 ------------- 517 ------------- 17,240		
Hg 546 1			
Tl 535 1	Green		
H(F) 486 7	---- 500 ------------- 600 ------------- 20,000		
Sr 460 8	Blue		
H(G) 430 8	---- 440 ------------- 682 ------------- 22,750		
Hg 404 6	Violet		
	---- 400 ------------- 750 ------------- 25,000		
Hg 365 0			
	Near Ultraviolet (Analytical range)		
	---- 230 ------------- 1305 ------------- 43,500		
	Far Ultraviolet		

Note the similarity of the limits of the visible range in terms of millimicrons and fresnel units.

(Owing to the subjective nature of color, the above figures are merely approximations.)

sion and the consequent inaccuracy of wave-length measurements (however, see Emery[53]). By increasing the number of prisms (Fig. 20), it is possible to increase dispersion, but with considerable sacrifice of brilliance. The dispersion of a chain of x identical prisms is x times the dispersion of a single prism.

The Spekker Steeloscope (manufactured by A. Hilger) is a portable spectroscope designed for rapid analysis of ferrous alloys

and is equipped with an ingenious comparison eyepiece for rough quantitative work (see Figs 21 and 44).

One of the most popular spectroscopes is the constant-deviation spectrometer shown in Fig. 23.   This device is direct reading and is very convenient for many purposes.
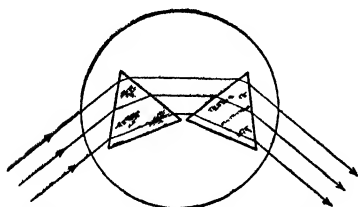
Fig 20 —A chain of two prisms.

18. Limits of Wave-length Range.—The visual spectroscope is obviously confined to use within the region of visual sensitivity 3,900 to 7,500 A, although it is possible to extend the lower limit slightly by use of ultraviolet fluorescing screens. Spectrographs, on the other hand, are limited only by the sensitivity of the photographic emulsion and the absorption of the optical system.   Recent photosensitizers[54,55] have made possible the photography of the far ultraviolet and
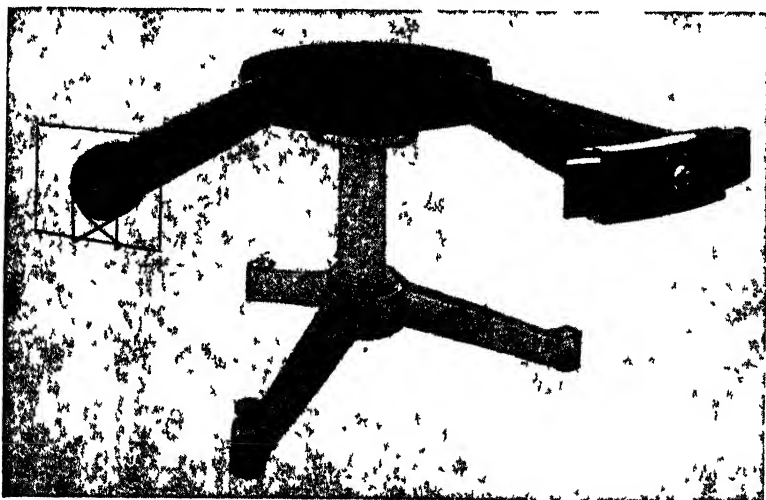
Fig. 21.—The Spekker Steeloscope   *(Courtesy of A. Hilger and Jarrell-Ash Company)*

infrared, so that the limiting factor is largely absorption due to prisms and lenses.   A list of practical transparency limits is given in Table 3.   Notice that for work in the far ultraviolet a vacuum spectrograph must be used, since air (oxygen) absorbs strongly in this region.

TABLE 3

Substance	Transparency Limit, A
Lithium fluoride	1,000–about 50,000
Calcium fluoride	1,250–about 90,000
Quartz	1,950–about 40,000
Air	Above 2,000
Glass	3,500–about 30,000
Sodium chloride	2,000–above 140,000

19. The Simple Prism Spectrograph.—In most cases, it is necessary to observe the spectra of transitory or flickering

FIG. 22.—A direct-vision spectroscope.
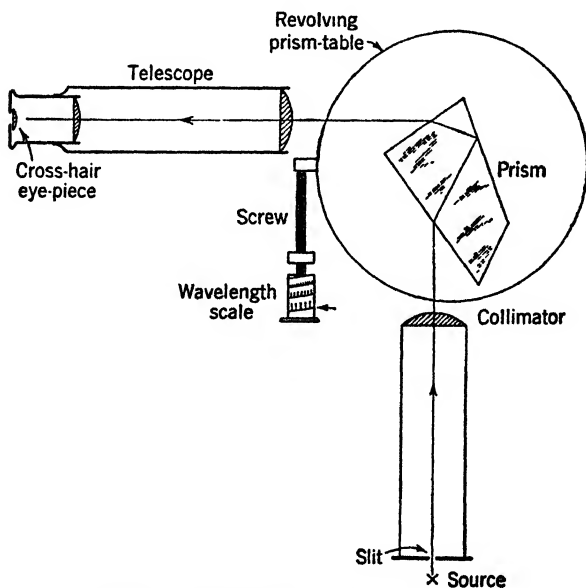
FIG. 23.—Constant-deviation spectrometer.

sources whose transient nature does not permit visual observation or measurement of more than one or two lines. It is also desirable, in general, to make observations in the ultraviolet region where the dispersion of a prism is greatly increased. Because of these two factors, the photographic method of spectral

observation is employed almost exclusively in chemical spectroscopy (however, see Kraemer[56]).

A simple spectroscope may be adapted for photographic use by mounting a camera in a suitable position, as shown in Fig 24 The position of the photographic plate is largely determined by
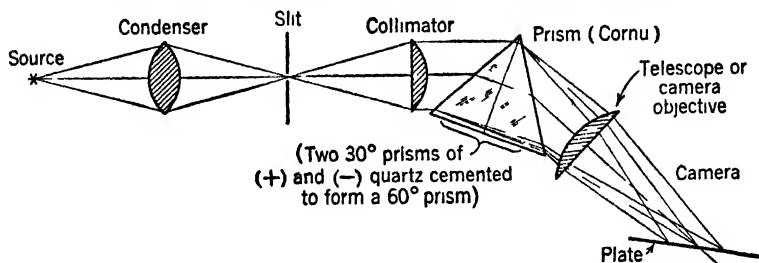
FIG 24 —Quartz spectrograph (Single glass prism is used for work in the visible region)

the degree of chromatic correction of the lens system. Complete linear achromatization of lenses is difficult, and most spectrographs are constructed with a slightly curved plateholder to allow for optical imperfections of the lens system. The spectral lines themselves usually show some curvature.
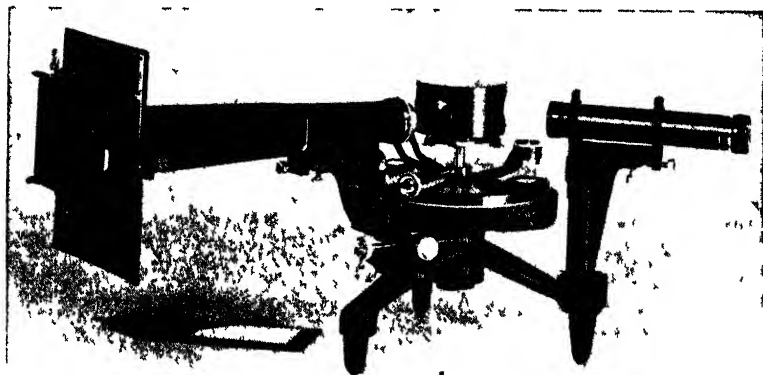
FIG. 25.—Spectrograph on spectrometer mounting. (*Courtesy of Spencer Lens Company*)

Spectrographs are usually not adapted spectroscopes (Fig. 25) but are constructed exclusively for photographic work (Fig. 26). Quartz lenses and Cornu prisms are generally used, the latter being made of two 30° prisms of quartz cemented so that the optical rotations cancel.

20. The quartz-prism Littrow spectrograph is shown diagrammatically in Fig. 28.   This type is the most popular of the high-dispersion prism instruments, one of the larger models (Fig. 29) having a dispersion of 1.54 A/mm. at 2,180 A and 7.1 A/mm. at
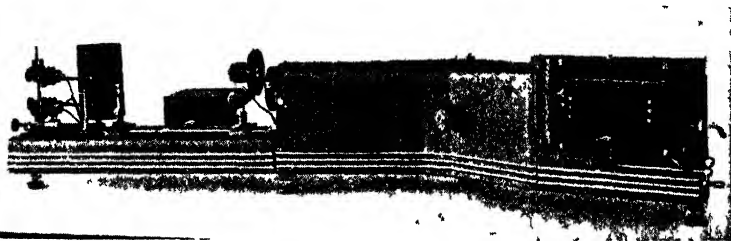
Fig. 26.—Medium quartz spectrograph.   (*Courtesy of Bausch & Lomb Optical Company*)

3,556 A.   Interchangeable glass and quartz systems are available, the former being preferred for work in the visible range because of its higher dispersion.   Since the rays traverse the prism twice, no correction need be made for the optical rotation of quartz.
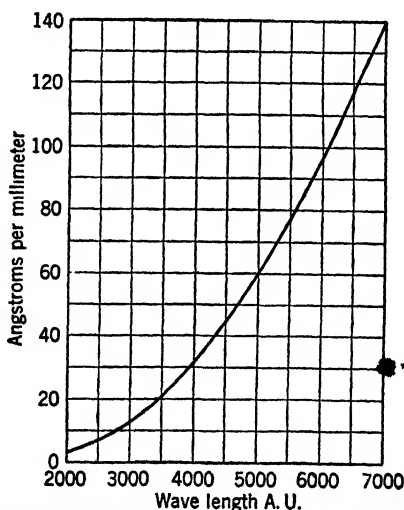
Fig. 27.—Linear dispersion of quartz spectrograph shown in Fig. 26.

21. Dispersion by a Plane Diffraction Grating.—A diffraction grating (Fig. 30) may be considered as a series of narrow slits separated by small opaque barriers.   The total width of a slit
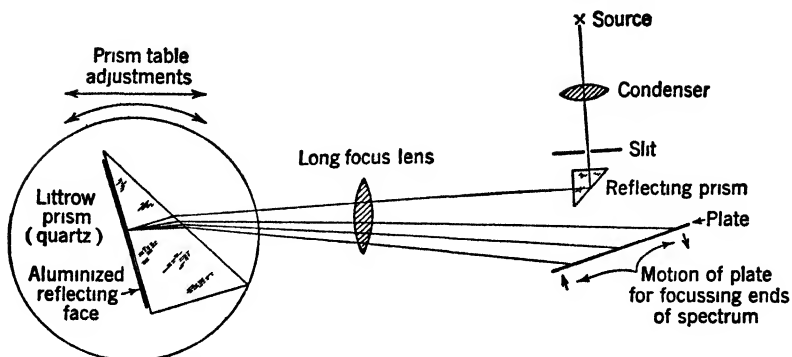
Fig. 28 —Quartz Littrow spectrograph   No correction for the optical rotation of quartz is necessary, since all rays traverse the prism twice.   The prism may be replaced by a glass prism, for work in the visible region, or by a concave grating, or by a plane grating
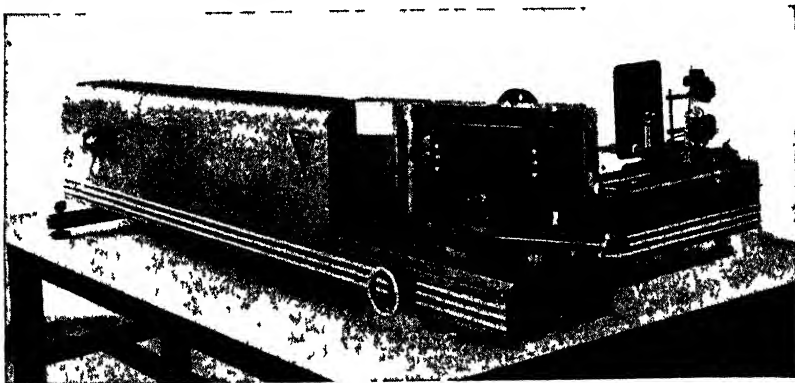
Fig. 29.—Large Littrow spectrograph.   (*Courtesy of Bausch & Lomb Optical Company*)
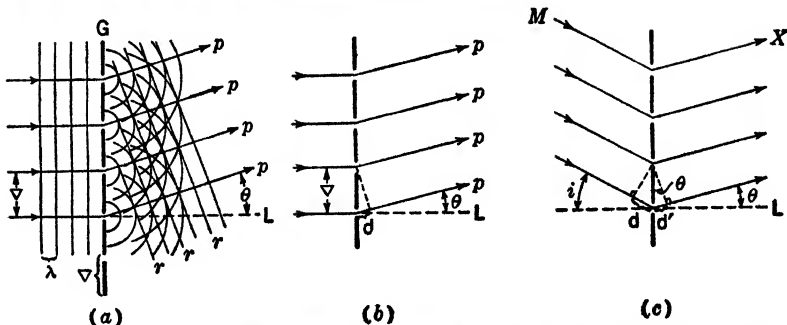
Fig. 30 —The plane transmission grating: (*a*) shows reinforcement of wavelets along lines *p*, (*b*) shows wave-front normals alone; (*c*) wave-front normals *M* of illuminating beam not perpendicular to grating surface.

plus a barrier is the grating constant ∇ which equals the reciprocal of the number of slits per unit length of grating.

Consider a plane wave front of monochromatic light of wave length λ impinging on a plane transmission grating. The light passes through each slit which then acts as though it were a source of wavelets spreading outward as shown. These waves are originally all in the same phase and will destructively interfere with one another along directions where the net phase difference given by d is not a whole number of wave lengths. In the figure, the normal lines p represent directions of propagation such that the phase difference d is in fact a whole number. These directions are normal to the wave fronts r which are made up of many wavelets of wave length λ originating at the slits of the grating.

If the wave-front normals p (Fig. 30b) make an angle θ with the normal L to the grating surface, then from the geometry of the situation $d/\nabla = \sin \theta$ whence $d = \nabla \sin \theta$. But if rays are propagated only when d is equal to an integral number of wave lengths, then $d = n\lambda = \nabla \sin \theta$ where $n = 1, 2, 3 \cdots$.

FIG. 31.—The plane reflection grating.

An illustration of the more general case is given in Fig. 30c where the value of the angle of incidence i is taken into account. The equation then becomes $n\lambda = \nabla (\sin i \pm \sin \theta)$ for a plane transmission or reflection grating (Fig. 31).

If the plane grating is illuminated with nonmonochromatic or heterogeneous light composed of many wave lengths, it may be inferred from the preceding equations that for each wave length there will be a corresponding value of θ, $i.e.$, the light will be dispersed to form a spectrum.

A further inference from these equations is the fact that more than one spectrum is formed by a grating. The angle θ may be measured clockwise from the normal, or counterclockwise; two sets of spectra are therefore produced. Further, n may be any integer, so there are also pairs of spectra of the second, third, etc., order, in addition to the *first-order* pair already considered. The higher order spectra ($n = 2, 3, 4 \cdots$) show greater dispersion

but are less brilliant.   Gratings may be constructed in such a manner that almost all the diffracted light is concentrated in the

first or second order (see Fig. 32c).   It is apparent from the equation that the various orders will overlap to some extent; thus a first-order line of 8,000 A will appear in the same place as a second-order line of 4,000 A and an exceedingly faint third-order line of 2,000 A.   In addition, the spectra may show "ghosts" or faint false lines which are due to defects in the grating.

22. The Concave Grating.—This is generally used in spectrograph construction because it needs no accompanying lenses.   Mathematical treatment of the optics involved is complicated (see Baly[36]), but it suffices to understand that the equation $n\lambda = \nabla (\sin i \pm \sin \theta)$ still applies (Fig. 33).   Since, in the drawing, the diffracted ray *GF* is on the opposite side of the normal *GN*, the sign of the equation will be negative.   If the

Fig. 32.—Enlarged diagrammatic cross sections of typical grating surfaces: (*a*) common ruling; (*b*) production of replica; (*c*) echelette ruling.

grating is mounted as shown, with the slit on a circle whose radius is half the radius of curvature of the grating, then the spectra
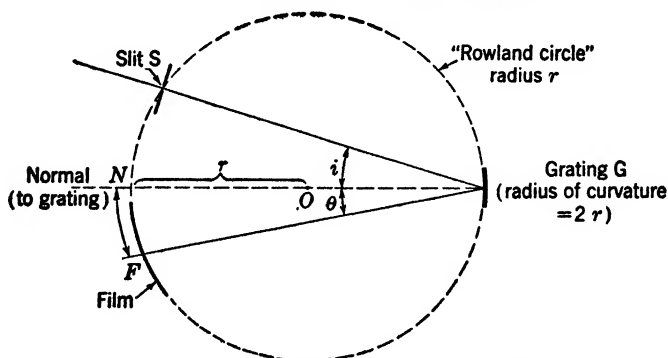
Fig. 33.—Optics of the concave grating spectrograph. θ = angle of diffraction for any wave length λ.

produced by the grating will be focused along the circumference of this so-called *Rowland circle*.   The film *F* may be moved to any

desired region of the circumference for observation of spectra ranging from the far ultraviolet to about 15,000 A in the infrared.

If i is kept constant, the dispersion of the grating may be obtained by differentiating the fundamental equation, which gives

$$nd\lambda = \nabla \cos \theta d\theta$$

or

$$\frac{d\theta}{d\lambda} = \frac{n}{\nabla \cos \theta}$$

If θ is replaced by its equivalent $NF/NG = s/2r$ radians in the original equation, then differentiation gives

$$\frac{ds}{d\lambda} = \frac{2nr}{\nabla \cos (s/2r)} = D = \text{linear dispersion}$$

Since $\cos (s/2r)$ varies very little with a change in s, it follows that the dispersion of a grating of this type is very nearly constant. Such dispersion is called *normal*, as opposed to the variable *prismatic* dispersion of a prism.

The resolving power of a plane or concave grating may be derived from theoretical considerations[57] from which $\lambda/d\lambda = nN$ where n is the order of the spectrum and N is the number of lines in the illuminated portion of the grating. This resolving power depends to a large extent on the quality of the grating as well, and useful values of D must be obtained experimentally. However, the simple equation given illustrates the fact that a wide perfect grating gives greater resolution than a small perfect grating. Despite this conclusion, it is considered better to mask imperfect portions of a grating and use a smaller perfect area in order to secure maximum resolution.

23. The manufacture of diffraction gratings is accomplished by the use of "ruling engines." These are automatic machines that cut a tiny wedge-shaped line (Fig. 32) into a glass or metal surface and then move a ten-thousandth of an inch or so and cut a parallel line. Great accuracy is required to maintain even cuts and perfect spacing. Gratings up to 120,000 lines per inch have been ruled successfully, but 30,000 lines per inch is the usual maximum.

The echelette grating (Fig. 32c) may concentrate as much as 80 per cent of the illumination in the first-order spectrum (or

any desired order) as compared with less than 20 per cent for other types.   Less expensive gratings are *replicas* of original rulings made by coating the latter with a plastic film, which is carefully stripped off and mounted on a suitable support.

Reflection gratings are usually "sputtered" with evaporated aluminum, which gives a stable polished surface whose reflecting power in the ultraviolet is higher than that of silver.

24. *Astigmatism* is that property of a concave grating which images a point source as a line.   This defect is serious for two reasons: (1) it lengthens spectral lines, their intensity being thereby reduced, and (2) it precludes the use of any device placed at the slit for the purpose of shortening the lines.   This latter situation is encountered in quantitative spectroscopy when a rotating spiral disk is placed in front of the slit (Sec. 34).   In most cases, the disk or other device may be placed a short distance away from the slit where it will function satisfactorily.   The correct distance is best determined experimentally.   For a treatment of the optics involved, see Baly[36] and also Dieke,[58] who discusses a remedy involving the use of cylindrical lenses.

25. Grating Spectrographs.[36,58,59,60]—The original mounting of Rowland is shown in Figs. 33 and 34.   It is not so popular as
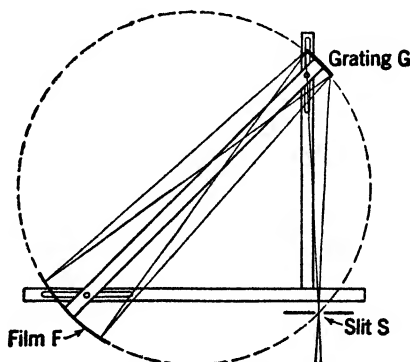
1 IG. 34.—Rowland mounting.   The slit is fixed.   Grating and film move together on sliding arm so that both lie on Rowland circle.

some of the other mountings described below because of its bulk and certain difficulties of adjustment.   The spectrum is nearly normal, however.   The similar mounting (not illustrated) of Abney has a movable slit and fixed plate.   The Paschen circular mounting is shown in Fig. 35.   Its principal advantage is the

ease with which the plate may be moved from one region to another.

Astigmatism is eliminated by the introduction of a mirror in the Wadsworth stigmatic mounting (Fig. 36), and the speed or
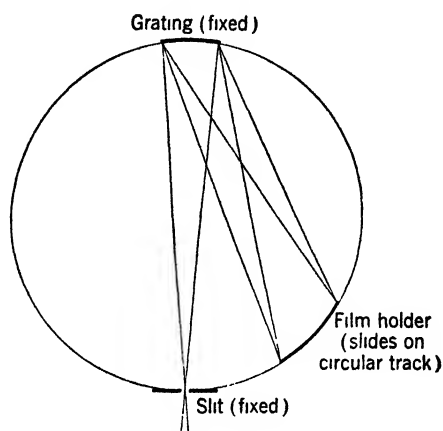
FIG. 35.—The Paschen mounting.
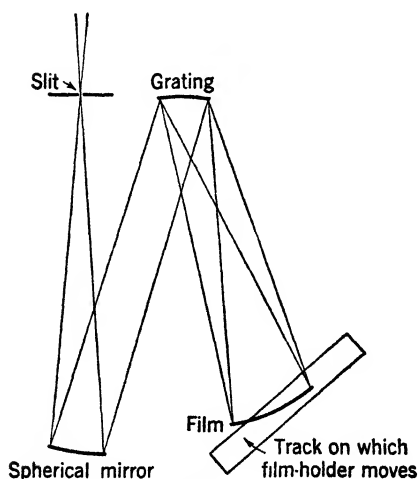
FIG. 36.—Wadsworth stigmatic mounting.

light-gathering power is increased. The instrument is bulky, however, and the focal curve is not quite circular.

By far the most popular are the Eagle mounting (Fig. 37) and its several modifications, e.g., Fig. 38. These mounts are com-

pact and, owing to the fact that the grating returns rays over nearly the same path, the astigmatism is slight.   The adjustment of the film and grating requires a complicated mechanical device, but this is hardly a defect.   Baly[36] cites the advantage of increased dispersion over the Rowland mounting and the greater range of wave lengths.   Dieke[58] gives an excellent discussion of the merits of this mounting as well as a summary of other methods.   Meggers[59] gives a more general discussion of several instruments.   A few excellent articles on spectrograph design
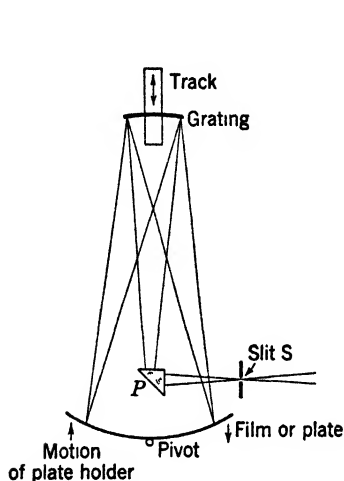
Fig. 37.—The Eagle mounting (Littrow type). *P* is a reflecting prism placed just above or below the rays diffracted by the grating.
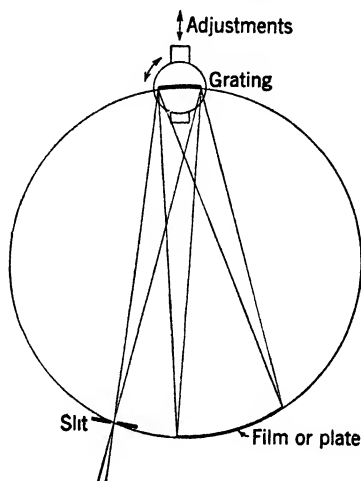
Fig. 38.—Modified Eagle mounting.

and construction and the testing of optical parts are given in references 61 to 66.

26. The choice of spectroscopic equipment depends naturally on the type of work that is to be done.   The concensus of opinion seems to be in favor of the grating rather than the prism instrument, and two convincing arguments in favor of the former are given by Harrison[67] and Slavin.[68]   The quartz Littrow prism (Fig. 28), however, has certain advantages, especially for quantitative work, such as absence of astigmatism.

If work is to be done on ferrous materials, high dispersion is necessary because of the complexity of the spectra of Fe, Ni, Co, Mn, Cr, etc.   Also, measurement of wave length is more accurate
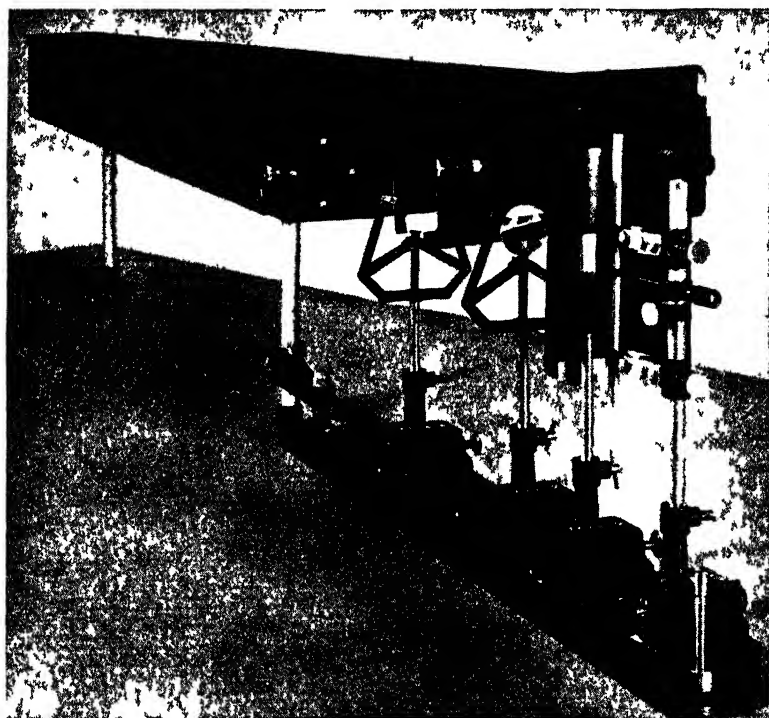
FIG 39 —The Cenco spectrograph.
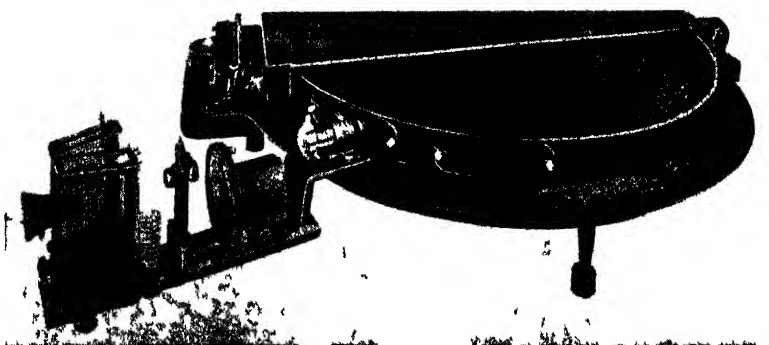
FIG. 40 —The A. R. L. spectrograph. Applied Research Laboratories. (*Courtesy of H. W. Dietert Company.*)

if the dispersion is great.   A spectrograph of low dispersion, say 15 to 20 A/mm., will cover a larger spectral range at one setting and is suitable for most nonferrous work.   The Cenco instrument (Fig. 39) with a dispersion of 16 A/mm. is one of the least expensive of the grating instruments and is well suited for such work.   The Dietert spectrograph (Fig. 40) is a more elaborate model with a dispersion of 7 A/mm. and the Baird Associates instrument (Fig. 41) represents further refinement, but with a particular view to industrial hard usage.   The 3-meter model
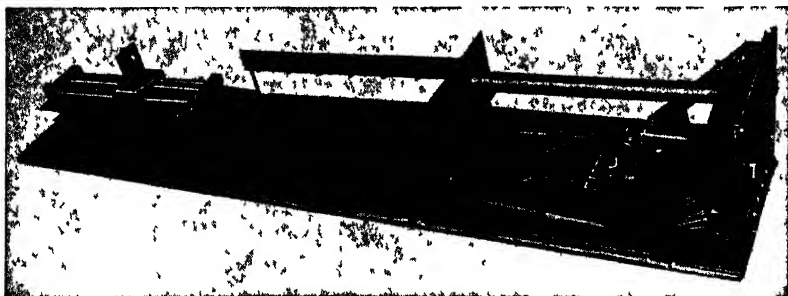
FIG. 41.—The Baird Associates concave grating spectrograph.   This view shows the instrument without its protective cover.   The grating holder and focusing mechanism are at the extreme left   All focusing operations are performed electrically and are controlled by switches located on the front panel. The slit and plateholder are mounted on the same panel.   (*Courtesy of the Baird Associates.*)

gives a first-order dispersion of 5 A/mm. and a fourth-order dispersion of 1.3 A/mm.

The spectrographs mentioned are representative of many types of instruments put out by several concerns in this country and abroad.   Manufacturers are generally qualified to recommend equipment for the particular requirements of the purchaser, and a wealth of information is available in catalogues (see especially the technical publications of A. Hilger[70]).

27. Photographic Processing.—The development and fixation of films or plates are dependent to some extent on the type of photographic emulsion and upon the degree of contrast desired. For qualitative work, where high contrast is required, a very vigorous quick-acting developer may be used.   Vincent and Sawyer[71] give a formula for a 30-sec. developer (Eastman 385 plates), but the Eastman D8 prepared developer is similar and almost as fast if used at four times the recommended con-

centration.   The D11 Eastman developer is slower in action but gives very good contrast.   In precise quantitative spectroscopy, the emphasis is placed on achieving a linear relationship between log intensity and density, rather than on contrast. Brode[10] recommends the ordinary M-Q tube developer for Eastman 33 plates.   Any commercial formula, recommended by the maker of the emulsion, will give satisfactory results. Whatever developer is used, the film or plate should be completely immersed in the solution, and the latter must be agitated as thoroughly as is feasible.   Temperature should not go above 20°C.   After development, the film is immediately immersed in a short-stop bath.   This may be simply 1 per cent acetic acid or, better, a solution of about two teaspoonfuls each of sodium bisulfite and powdered chrome alum in 1 liter of water, acidified with a few drops of sulfuric acid.   The latter short stop hardens the emulsion and thus aids drying, but it must be made up fresh each time.   Vincent and Sawyer recommend a 20 per cent solution of chrome alum for this step.

After agitating in the short stop for 20 or 30 sec., the film is transferred to the fixing bath.   This may be either a commercial acid hypo made up to about $\frac{2}{3}$ the recommended strength or, preferably, the mixture given by Vincent and Sawyer: 300 g. hypo, 60 g. ammonium chloride, and 45 g. sodium bisulfite (dry) dissolved to make 1 liter.   If speed is the primary aim, the film may be removed from the fixing bath immediately after it clears.   Greater permanence may be obtained by soaking for about 10 minutes.

The film may be washed in a flat jet of water, originating from a slotted orifice, or it may be allowed to soak in running water.   The jet method gives sufficient washing in 20 or 30 sec., but again, if permanence and clarity are desired, a 10- or 20-minute wash is recommended.

Drying is best accomplished by blowing a stream of heated air over the film.   An ordinary hair drier is a good makeshift. Addition of a trace of a wetting agent to the developer and hypo is said to increase their speed of action and to facilitate subsequent drying.

A few symptoms of the more usual photographic difficulties are listed below.

1. Dark areas on the film—leaky camera.

2. General fogging of the film—stray light in the spectrograph or insufficient fixing.

3. Streaky film—insufficient agitation during development.

4. Overdevelopment, graininess, reticulation, and pinholes—temperature of the developer too high.

5. Softness of the emulsion—insufficient hardening or temperature of the fixing bath or wash water too high.

6. Film warping and turning brown in time—insufficient fixation or too rapid washing. Hypo should be rejected when it feels "slimy" or foams excessively on pouring.

Developers keep best in full bottles that are kept cool and protected from light. The life of the hypo is greatly prolonged by the addition of a drop of chloroform or a few crystals of sodium furoate to prevent bacterial growth. Unless the solutions are in constant use, it is worth while to make them up fresh for each occasion.

28. Identification—Measurement of Wave Length.—The identification of metals may be accomplished either by measuring wave lengths of several lines and comparing with tables, or comparing the spectra with those obtained from known samples. The latter may be separate spectrograms, filed according to the sample, or if a spectrograph of high dispersion is used, the entire set of comparison spectra may be obtained on one film or plate through the use of R.U. powder. This powder is a suitably balanced mixture of 50 of more elements such that each gives its more important lines when excited in an arc. The abbreviation R.U. indicates *raies ultimes*, or those lines which are the last to disappear as the concentration of the metal is decreased. These lines are also referred to as the "sensitive lines."

Not only are the sensitive lines valuable for purposes of identification, but the spectrum of each element contains characteristic patterns of lines, *e.g.*, a strong triplet at a certain wave length, etc., by which the element may be identified at a glance by an experienced analyst.

Attention should be called to the excellent tables of Twyman and Smith,[72] who have compiled lists of sensitive lines for arc and spark as well as data on the effect of concentration. Their book gives a great deal of pertinent information on the theory and technique involved.

SEC. 28]   SPECTROCHEMICAL ANALYSIS

Bardet's "Atlas of Arc Spectra"[73] gives 48 enlarged prints of spectra referred to the iron spectrum, and various other works of similar type are available.[74-77]

Determination of purity is easily accomplished by photographing the spectrum of a sample of known purity beside that of the suspected sample. For this purpose and for comparisons in general, the Judd Lewis Comparator is a very useful tool. This
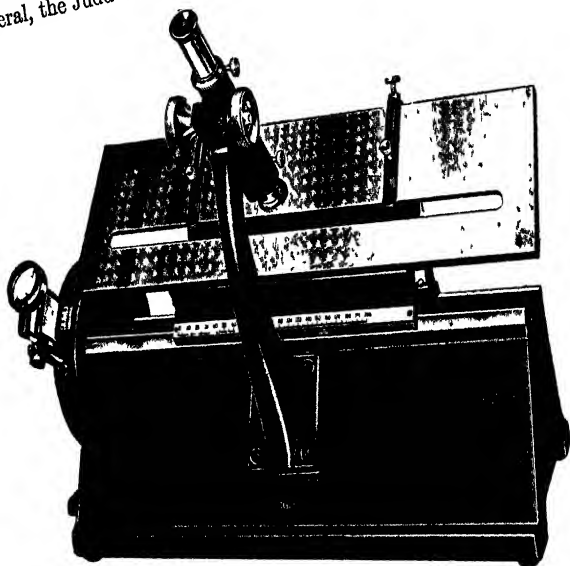
FIG. 42.—Measuring microscope. *(Courtesy of Gaertner Scientific Company.)*

optical device (manufactured by A. Hilger) brings two spectra into adjoining positions in a divided field of view.

The actual measurement of wave length may be carried out in a number of ways. Perhaps the simplest is direct measurement and interpolation carried out on the film or plate. A 10× magnifier with a built-in transparent scale divided to tenths of a millimeter is used for measurement over a range of 2 or 3 cm., or a low-power microscope fitted with an ocular micrometer may be used. Measurement over longer distances may be made

by means of a measuring microscope (Fig. 42) mounted so that it travels along a micrometer screw.   An alternative and popular method is the projection of an enlarged image of the spectrum on a horizontal screen where it may be measured with a ruler.[75,78]

Wave lengths of unknown lines are measured by interpolation from known lines as in Fig. 43.   If the spectrum is normal, as from a grating, the interpolation is linear and the wave length of the line marked by the arrow is obtained by measuring the
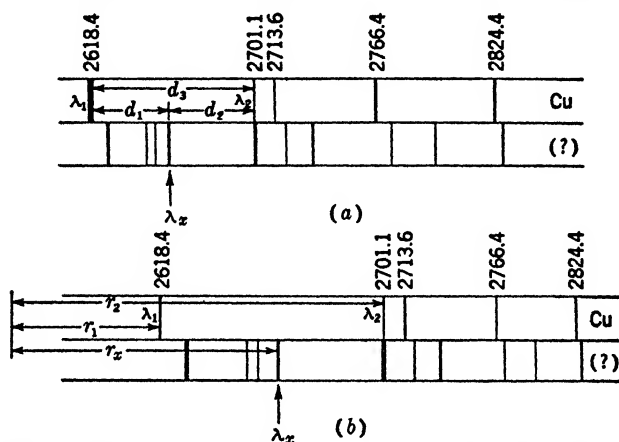
FIG. 43.—Measurement of wave length: (a) normal spectrum; (b) prismatic spectrum.

distances d and d_2 to the comparison lines λ_1 and λ_2 of the reference spectrum.   Thus

$$(\lambda_2 - \lambda_1):d_3::(\lambda_x - \lambda_1):d_1:(\lambda_2 - \lambda_x):d_2$$

or

$$\lambda_x = \left(\frac{\lambda_2 - \lambda_1}{d_3}\right) \cdot d_1 + \lambda_1$$

The term $(\lambda_2 - \lambda_1)/d_3$ has a constant value throughout the spectrum if the dispersion is normal, and this value need be determined only once and set equal to D.   Then the interpolation equation becomes simply $\lambda_o = Dd_1 + \lambda_1$.   It is a good idea to determine D for several regions of the spectrum to check the normality, and to check the value for each film or plate, because of possible distortion of the latter through shrinkage.

If the dispersion is prismatic (Fig. 43b), two alternative methods of interpolation are presented.   The first is to assume.

normality of dispersion over very short ranges, which is a valid assumption only when the dispersion is very large. The general, exact method is that due to Hartmann[79] and involves the dispersion equation

$$\lambda_x = \lambda_o + \frac{c}{d_x - d_o} \qquad \text{or} \qquad \lambda_x = \lambda_o + \frac{c}{d_o - d_x}$$

where λ_o and c are constants obtained by solving three equations where λ_x, d_x, and d_o are all known. Meggers[79] gives a simple method of solving the above-mentioned simultaneous equations and also points out a mathematical simplification when many wave lengths are to be read.

Many instruments are fitted with a built-in transparent chart which automatically prints a wave-length scale on the photographic plate or film on which the spectrum is registered. Such a device is seldom accurate enough for actual measurements, but it aids in the location of desired lines.

QUANTITATIVE SPECTROSCOPY

29. According to Nitchie,[20] quantitative spectrochemical analysis possesses advantages that render the method particularly suitable for quantitative estimation of traces, impurities, or minor constituents whose determination by chemical methods is not feasible; for rapid estimations where chemical analysis is feasible but too slow; and for determination of the approximate composition of samples that are too small to be dealt with by chemical means.

Generally speaking, quantitative spectrochemical analysis would not be used for determination of major constituents in a large sample, but would undoubtedly be used in preference to any other method for analysis of metallic traces, present in amounts ranging from less than 0.001 to about 1 per cent. The range 0.01 to 5 or 10 per cent is fairly well handled by chemical colorimetry (Chap. III), but spectroscopic methods present the advantages of specificity and the absence of "wet manipulation." This latter factor becomes a major source of error in chemical analysis of traces, owing to the necessary bulk of the sample, the tendency of traces to coprecipitate with other precipitates, and the solubility of small amounts of precipitate because of the necessarily large volume of solution. Although

the precision of quantitative spectrochemical determinations is rarely better than 5 per cent, the errors of conventional chemical methods are usually as great or greater in the low concentration range of 0.001 to 1 per cent.

Historically, the development of quantitative emission spectroscopy dates from the publications of Hartley,[3] who worked out tables correlating the concentration of solutions with the number of spectral lines observed in the spark spectrum. The work of Hartley, Pollok and Leonard, de Gramont, and others is ably reviewed in a compilation of spectroscopic data by Twyman and Smith.[72] All three methods of excitation, flame, arc, and spark, have been used successfully.

30. The Principle of Relative Intensities.[51,82]—The basis of modern quantitative spectroscopy is the measurement of the intensity of a spectral line due to the sought-for constituent, *relative* to a line due to a second component that is present in a constant amount. This second component, or *internal standard*, may either be added to the sample, or be an original principal constituent. In the latter case, the percentage of the principal constituent is sufficiently high so that it may be considered as independent of the percentage of the desired constituent.

In order to suppress the effect of other materials that may be present in the sample, it is common practice to add a relatively large amount of some inert "base" or "buffer." Addition of the base makes a series of differing samples more nearly alike, which is desirable because great differences in qualitative composition may affect the relative intensities of the lines.[83,84] The alumina-silica base, referred to in Sec. 11, and also mixed potassium and ammonium chloride, sodium nitrate, and many others are frequently used. Obviously, if the samples are alike at the beginning and possess a common principal constituent, the addition of a buffer is unnecessary.

A third factor that affects quantitative measurements is the relative volatility of the various components of the sample. Two methods are used to eliminate this difficulty. One is to make several short exposures, the sample being replenished each time. The other, due to Slavin,[85] is to burn the sample completely in a 2- to 4-minute exposure. These two methods necessarily apply only when the arc method of excitation is employed. (The Preuss[86] moving-plate technique, usually

employed for the investigation of volatility may also be used for actual quantitative estimations. The spectrum is photographed on a plate that moves vertically at a rate of a few tenths of a millimeter per second. The length of the lines furnishes information as to the persistance of the emission and hence the volatility.)

31. Homologous Lines.—The reason for measuring the intensity of a given spectral line relative to the intensity of a line of the internal standard is to cancel out the effect of variations in the spectroscopic procedure. Thus the intensity of the given line depends on the excitation of the source, the exposure time, the adjustment of the instrument, the photographic processing, and a score of other factors. The intensity of this same line relative to a suitable reference line, however, will be independent, within limits, of all these factors, because the reference line will be affected simultaneously in just the same way.

The suitability of the reference line depends on the very fact that it must respond to varying conditions in just the same way as the line that is compared with it. A pair of lines that fulfills this condition is called a *homologous pair*.[87] The choice of a homologous pair may be made on the basis of experiment or by consulting the voluminous literature on the subject (see especially Gerlach and Riedl,[88] and Lundegardh[17]). Note that both lines must be due to either neutral atoms or ions. If one line was atomic and the other ionic, then an increase in the exciting energy would enhance the ionic line more than the atomic line (see Sec. 6).

A second criterion for the suitability of the reference line is that it have nearly the same intensity as the given line. Since the intensity of the given line varies with the concentration of the sought-for metal, the intensity of the reference line should equal that of the given line somewhere within the limits of the concentration range observed. It follows, therefore, that if the reference line is due to a principal constituent of the sample, then it must be chosen from among the weaker lines in the spectrum of the principal constituent. If, on the other hand, the internal standard is added to the sample in a small known amount, then one of the stronger lines may be chosen as the reference line.

32. The Spekker Steeloscope.—A very simple and, successful application of the principle of relative intensity is made in

visual spectroscopic analysis of ferrous alloys with the Spekker Steeloscope (Fig. 21).   This high-dispersion prism instrument is fitted with a split-field eyepiece (Fig. 44) which divides the spectrum of the sample into two adjoining horizontal halves. The lower half of the spectrum may be moved laterally by rotating one of the components of the eyepiece.   To obtain a quantitative analysis of a sample of alloy, the latter is placed in an arc and its spectrum is studied carefully.   A line due to the desired constituent and a suitable, somewhat brighter line due to the major constituent are chosen as described above.   The lower part of the spectrum is then moved until the reference line is

Field of insta eyepiece
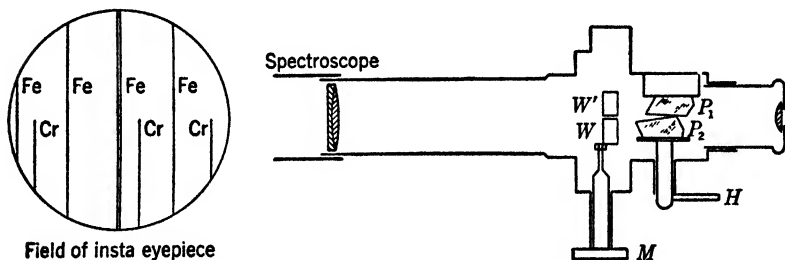
Fig. 44.—Hilger Insta eyepiece (Steeloscope).   Prisms P_1 and P_2 divide the spectrum horizontally into halves.   Prism P_2 may be rotated by means of handle H, to bring any desired line in the lower half of the spectrum into coincidence with a reference line in the upper spectrum.   The neutral wedge W is actuated by a rack-and-pinion movement controlled by knob M.   The compensating wedge W' permits adjustment of the zero setting and facilitates complete matching of the two halves of the field of view.

directly below the chosen line, and the brightness of the reference line is then diminished by means of a neutral-tint wedge of dark glass until the two lines are matched in intensity.   The scale of the graduated wedge is read, and the reading is located on a previously prepared graph of wedge reading vs. percentage. Values of the percentage of the desired metal may be found in this way with an asserted accuracy of the order of 5 per cent.[89]

33. Two simple spectrographic procedures, which may be used for rough quantitative analyses, are included here because of their simplicity and the fact that no special equipment is necessary, although their accuracy is usually not better than about 10 per cent.   The procedure of Gerlach[82] and Schweitzer[81,87] involves preparation of a series of mixtures similar in composition to the sample but containing known percentages of the desired metal and the internal standard.   The spectrum of each mixture

is then photographed under identical conditions and is carefully examined for lines of equal intensity. The example cited by the authors is the analysis of solder for tin and lead, the latter being the principal constituent. It was found that when the tin was present to the extent of 5 per cent the tin line at 2,422 A was equal in intensity to the lead line at 2,412 A. At 0.6 per cent tin, the tin line at 2,572 A matched the weaker lead line at 2,657 A, and at 0.04 per cent tin, the strong tin line at 2,707 A had become equal to the weak lead line at 2,657 A. A table is drawn up from a series of such observations, and by noting the equality of line pairs, it is possible to determine percentage with a considerable degree of accuracy.

A second simple method is that of Nitchie.[20] The principle of this procedure is to compare the intensity of a given line due to the metal whose percentage is desired with the same line in a series of adjoining spectra of standard samples. The standard mixtures are prepared as above, and their spectra are photographed under identical conditions on a single plate, but with a space between each spectrum. The spectrum of the unknown sample is photographed under the same conditions on a separate plate, and the blackening of a suitable line is compared with the blackening of the same line in the series of reference spectra. In this way, the approximate percentage may be estimated. For the final determination, the spectrum of the unknown sample is photographed between the spectra of the two reference samples whose compositions are closest to that of the unknown, and the line intensities are again compared. In expert hands, the method is capable of considerable accuracy, but great pains must be taken to ensure identical conditions of exposure, development, etc.

34. The log-sector method[10,90,91,92] is as simple as the two preceding methods, but requires the auxiliary equipment shown in Fig. 45. This so-called log-sector disk is placed directly in front of the slit of the spectrograph so that it casts a sharp shadow on the spectrum. The slit should be slightly longer than the maximum distance h in Fig. 46, and may be opened to about 0.02 mm. or more. The condensing lens may be removed or placed very close to the sector disk so that uniform illumination is attained, or a cylindrical lens may be used as the condenser, or lastly, a very thin lens may be placed on the slit itself. Since

the exposures will be 1 to 5 minutes, not a great deal of light is required. If a grating spectrograph is used, the log sector must be placed at the horizontal focus of the grating (see Sec. 24).

The obvious effect of rotating such a disk in front of the slit will be to attenuate the degree of b l a c k e n i n g of a photographed line, thus giving the appearance shown in Figs. 46 and 47. In this way, the height of a line becomes a measure of the intensity. If the attenuation is logarithmic,

Fig. 45.—Log-sector disk. (*Courtesy of Central Scientific Company.*)

then the length of a line is directly proportional to its log intensity

Equation of spiral:
$$\log \frac{\omega}{\pi} = K + K'h$$
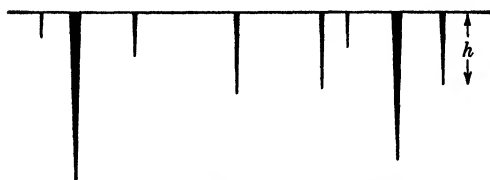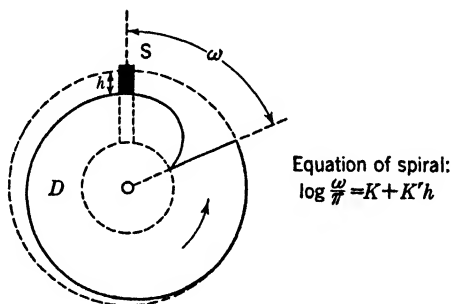
Fig. 46.—Use of log-sector disk.

S = slit of spectrograph
D = disk
h = height of illuminated portion of slit at any instant
ω = angular distance of zero point of sector from slit
KK' = constants

because the response of a photographic emulsion is also logarithmic (Sec. 35). Note that the log-sector disk acts as a

logarithmic neutral wedge, and indeed the use of quartz wedges "sputtered" with metal has been proposed as a substitute.[93,94]

The quantitative analytical procedure requires first the preparation of several standard mixtures containing constant
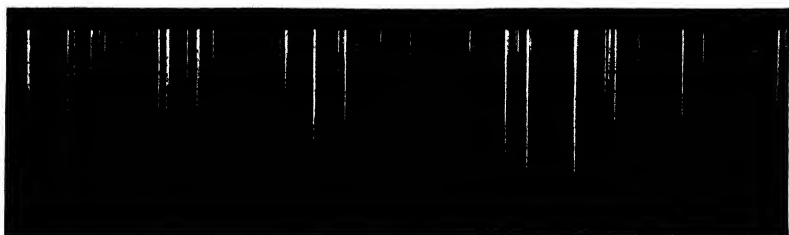
Fig. 47.—Log-sector spectrogram.   (*Courtesy of G. R. Harrison.*)

known percentages of the internal standard and varying known percentages of the metal to be determined. The internal standard is selected on the basis of the homologous-pair principle discussed above. After photographing the spectra of these standards, using the sector disk, etc., the heights of homologous lines are measured with a scale magnifier graduated in tenths of a millimeter. A considerable improvement in the accuracy of this measurement is claimed for the device described by Wilhelm,[95] and a method of double-printing the negative on high-contrast emulsions is recommended by O'Brien.[93]   High contrast ensures sharpness of the ends of the wedge-shaped lines.
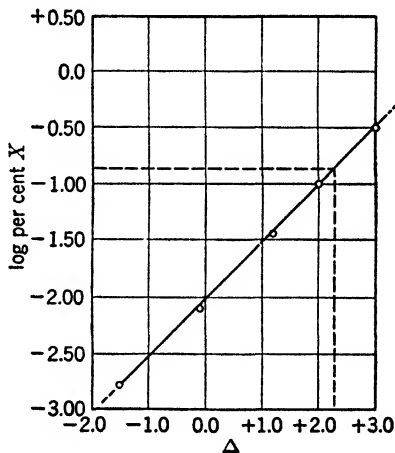
Fig. 48.—Working curve, log-sector method.

The algebraic difference between the heights of the two lines is then plotted against the percentage of the desired constituent or the log of this percentage (Fig. 48).   The analysis of a series of unknowns may then be referred to this working curve. Note that small variations in exposure and processing are canceled out by this method.   An additional advantage is that the working curve may be plotted on logarithmic paper to give a nearly

straight line[92] having a 45° slope.   This eliminates the need of
preparing a lengthy series of standard mixtures.

35. Characteristics of the Photographic Emulsion—Densitometry.—Before introducing the photometric methods of quantitative spectrochemical analysis, it is necessary to digress for a moment and consider the response of a photographic film or plate to variations in spectrum line intensity.

The degree of blackening of a photographic image may be described in terms of the difference between the intensity of a
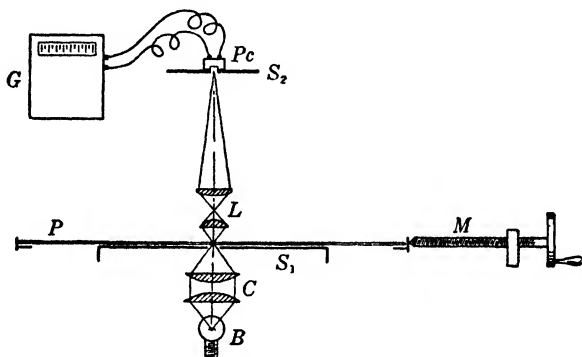
Fig. 49.—Spectrum line photometer (schematic).
B = concentrated filament bulb run at constant voltage
C = condenser
S_1 = shield with 1- or 2-mm. slit
P = spectrogram mounted on sliding carriage
M = micrometer screw which moves carriage
S_2 = screen on which image of spectrogram is focused
P_c = photocell mounted behind slot in screen
L = projection microscope
G = galvanometer

ray of light transmitted by the clear film and the intensity of the ray when it has passed through the blackened image.   Measurement of this transmitted intensity is generally carried out by means of an apparatus shown schematically in Fig. 49.   The purpose of the micrometer screw is to permit moving a spectral line laterally across the slit so that the point of maximum blackening (minimum transmission) may be located.   The galvanometer reading at this point (d_1) subtracted from the galvanometer reading for the clear film adjoining the line (d_0) will be referred to as the blackening B of the spectral line [density $= \log (d_0/d)$].

The relationship between the actual intensity of the spectral radiation and the blackening of the photographed line is shown

in Fig. 51. The intensity is expressed in arbitrary units which are simply the numbers of the steps on a logarithmic step wedge
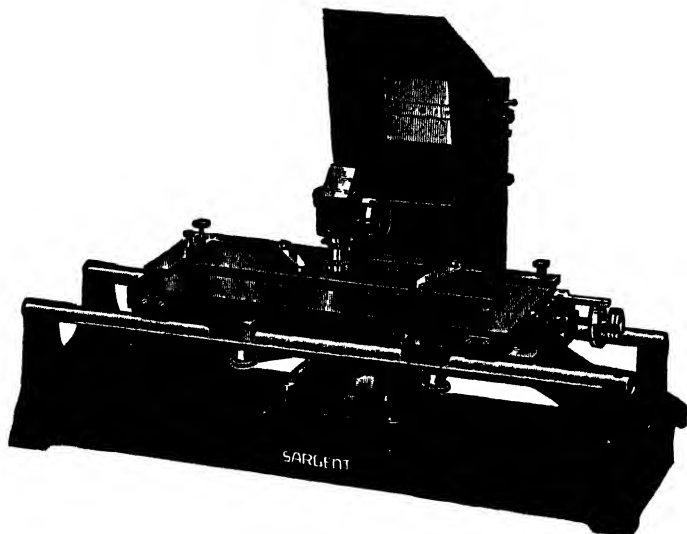
Fig. 50.—Spectrum line photometer. *(Courtesy of E. H. Sargent & Company.)*

which is used to construct the graph. The wedge may be a small strip of film which has been exposed in steps such that the intensity transmitted by the progressive steps varies logarithmically The graph of Fig. 51 may be constructed by contact printing such a wedge on an unexposed portion of an undeveloped spectrograph film. The film is then developed, and the blackening or density of each photographed step is measured with a photometer. These values are then plotted against a linear scale corresponding to the number of steps in the wedge.

Since the shape of the curve varies slightly with wave

Fig. 51.—Characteristic curve of photographic emulsion. (The so-called "*H* and *D*" curve used in photography is similar in shape, but the ordinate is density.)

length, it is better to place the wedge over a long spectrograph slit

and expose to a copper or iron arc. Each spectral line is then a reproduction of the wedge, and the characteristic curve may be plotted for light of any desired wave length by measuring the
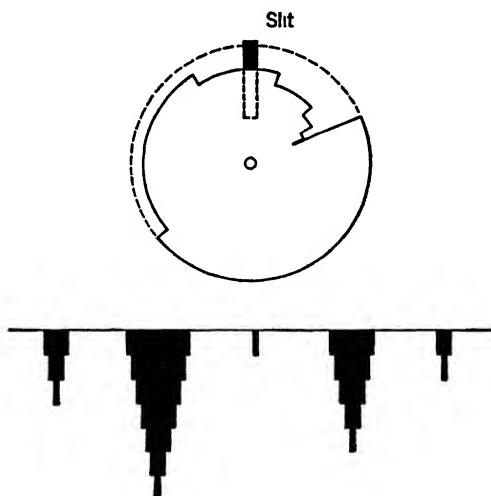
Fig. 52.—The step-sector disk and its effect.

blackening of each portion of the line. The step-sector disk (Fig. 52) is generally used in preference to a wedge (Fig. 53).

Not only does the shape of this curve vary with wave length, but also with the nature of the developer and the time of develop-
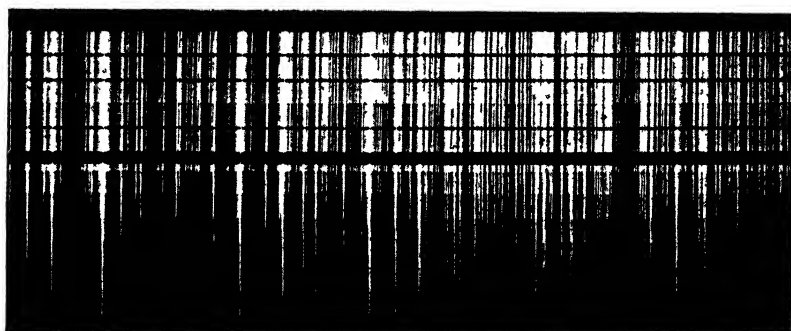
Fig. 53.—Use of the step-sector disk.   (*Courtesy of G. R. Harrison.*)

ment. The slope of the straight portion of the curve varies with the contrast of the emulsion; the greater the slope, the greater the difference in darkening for a given difference in intensity. Another interesting property of the emulsion is that

darkening varies with the intermittency of the illumination; thus ten 1-sec. exposures do not produce the same darkening as one 10-sec. exposure. A flickering illumination may therefore give rise to anomalous darkening effects unless the frequency is high. This factor is taken into account in the log-sector method where a rapidly revolving (1,200 r.p.m. or more) disk is specified. The disk is usually run by a constant-speed motor. Excellent general discussions of photographic problems are given by Strock,[96] Scribner,[97] Harrison,[98] and Smith.[99]

To return to the photometer illustrated in Fig. 19, it is apparent that the optical system is that of a microscope, the photocell being placed in the plane of the real image formed by the objective. Thorndike[100] gives directions for converting a microscope into a simple microphotometer by the addition of a few simple accessories and a photocell. Other more complicated devices are described in the literature.[99,101,102] Brode[10] mentions the use of a projection lantern and screen, with a photocell placed behind a slit in the screen.

36. The photometric method of quantitative analysis is an extension of the log-sector method already described. In the photometric method, however, the intensity of a pair of lines is compared by measuring their respective blackenings with a photometer. The intensities are then calculated graphically from the blackening values by means of the characteristic curve of the emulsion, and the *ratio* of these intensities is plotted against the percentage or log percentage of the desired component to give the working curve. Descriptions of the general procedure are given by Scribner,[97] Thomson and Duffendack,[103] Wolfe,[104] Gerlach and Schweitzer,[87] and Smith.[91] A simple device that is of great assistance in calculating intensity from blackening is described by Owens.[105]

If great accuracy is desired, it is advisable to use the logarithmic step sector (Fig. 52) in conjunction with the photometric method. The step sector serves the same purpose as the logarithmic neutral wedge mentioned above and divides the spectral lines into a series of steps. It is then possible to compare the intensities of the homologous lines directly at the levels where they show nearly equal darkening. This procedure is always recommended because the accuracy of a photometer reading varies inversely with the ratio of the line intensities, which

should not be larger than two or three. When larger intensity ratios are to be measured, the photometric comparisons are made on a step spectrum at different levels and multiplied by the corrected step ratio.

In case the background of the spectrum is quite perceptible, it is necessary to correct the observed line-intensity ratio by introducing factors i_x and i_y, which represent the measured background intensities. The line intensities I_x and I_y are then obtained from the observed line-intensity ratio which is given as $(I_x + i_x)/(I_y + i_y)$ (see also Strock[37]).

37. The Working Curve.— Whichever of the preceding methods is employed, the data obtained must be put in a useful form. In the case of the log-sector method, the *differences* between the lengths of the lines for a series of prepared samples are plotted against log percentage composition (Fig. 48), whereas in the photometric method, the log *ratios* of the corrected intensities are plotted against log percentage composition (Fig. 54). By measuring the corresponding difference or ratio for the unknown sample, its composition may be read directly from the working curve.

Fig. 54.—Working curve—photometric method.

38. Summary and Examples of Quantitative Procedures.—The first step in preparing for a quantitative spectrographic determination is a preliminary qualitative spectrographic analysis and its interpretation. The procedure then resolves itself as follows:

1. Choice of source, method of preparing the sample, and nature of the buffer or base mixture, if used. It is a good idea to make up the base mixture so that it is qualitatively similar to the unknown, but, of course, containing none of the sought-for constituent. A "blank" spectrogram should be run to establish the absence of the latter.

2. Choice of the homologous pair and the internal standard, determining the optimum percentage of the latter

3. Preparation of standard samples, made by mixing a known amount of internal standard into the base and dividing into two weighed portions. To one of these, a measured amount of the desired element is added so that its percentage will be greater than required. This portion is then diluted with the second portion of the base to give a series of standards.

4. Preparation of the working curve from these standards, this curve being used to determine the percentage in the unknown. Note that fewer standards are required for the log-sector and photometric methods than for the method of Nitchie or the original method of Gerlach and Schweitzer.

The following skeleton example illustrates the calculations for the log-sector and photometric procedures: Assume that the metal X is to be determined and that the metal Y has been chosen as an internal standard. The homologous pair λ_x and λ_y have been shown to be suitable, and a series of standard mixtures has been made up. Table 4 gives the experimental results obtained by the log-sector method. The working curve shown in Fig. 48

<center>TABLE 4 —LOG-SECTOR DATA</center>

Mixture	Concentrations			Length of lines, mm		
	% X	log % X	% Y	λ_x	λ_y	Δ
1	0 0016	−2 800	1 0	7 8	6 3	−1 5
2	0 008	−2 100	1 0	6 4	6 3	−0 1
3	0 039	−1 403	1 0	5 2	6 4	+1 2
4	0 100	−1 000	1 0	4 2	6 2	+2 0
5	0 316	−0 500	1 0	3 3	6 3	+3 0
6	0 0		1 0	0 0	6 3	+6 3
Sample	?	?	1 0	4 8	6 1	+2 3

is constructed from this data. The value of Δ given for the sample corresponds to a log per cent X of -0.860 or $\bar{1}.140$, hence the percentage of X will be 0.13.

The calculations for the photometric method are so similar that they will merely be indicated. The first step is to construct a table of the experimental data such as Table 5. The blackenings of the X line and the Y line are the photometer readings for the two lines subtracted from the reading for the clear film. The intensity values I_x and I_y are read from the characteristic curve of the emulsion as determined with a step wedge, slit, or

sector (see Sec. 35). The logarithm of the ratio I_x/I_y is then plotted against the logarithm of the per cent X. The working curve so obtained is shown in Fig. 54.

TABLE 5.—FORM FOR THE PHOTOMETRIC METHOD

Mix-ture	Concentrations			Blackening of lines (photom-eter reading for clear film $= i$)		I_x	I_y	$\dfrac{I_x}{I_y}$	$\log \dfrac{I_x}{I_y}$
	$\% X$	$\log \% X$	$\% Y$	B_x	B_y				
1 2 3 etc.									

39. Other Methods of Quantitative Spectroscopy.— An extension of the preceding photometric or log-sector method was developed by Foster, Langstroth, and McRae.[107] Briefly, it consists of measuring the intensity of some chosen line of the sought-for material, then determining the intensity of that line after successive additions of small known amounts of the sought-for element. Graphical extrapolation gives the original amount present.

The Barratt twin-spark method[108] employs two spark sources run in series, whose spectra are photographed side by side or partly superposed. One spark is between electrodes of pure substance or a sample of known composition; the other is between electrodes whose composition is desired. By altering the intensity of the "known" spectrum by means of a Nicol prism photometer, the intensity of two lines may be rendered equal. The amount by which the intensity of the "known" spectrum must be reduced is a measure of the concentration ratio.

Triché[109] uses a twin spark produced by sparking the known and unknown electrodes onto opposite sides of a metal plate which divides the slit aperture horizontally. The purpose of

the twin-spark procedure is of course to secure freedom from variation in the source, since the variations of the two sparks must be identical.

The very simple method of Nitchie[20] has already been mentioned. For other methods, see Hasler and Lindhurst,[110] Scheibe and Schnettler,[111] Strock,[37] and Wendt and Heun.[112]

40. General References.—For the sake of convenience, some of the more inclusive references, already mentioned in this chapter, are listed together.

<div align="center">TEXTS ON SPECTROCHEMICAL ANALYSIS</div>

"Spectroscopy," by E. C. C. Baly (three volumes), Longmans, Green & Company, New York, 1905–1927.

"Chemical Spectroscopy," by W. R. Brode, John Wiley & Sons, Inc., New York, 1939.

"Chemische Spektralanalyse," by W. Seith and K. Ruthhardt, Verlag J. Springer, Berlin, 1938.

"Clinical and Pathological Applications of Spectrum Analysis," by W. Gerlach and W. Gerlach, A. Hilger, London, 1934.

"The Practice of Spectrum Analysis with Hilger Instruments," by F. Twyman, A. Hilger, London, 1935.

"Spectroscopy in Science and Industry," by S. J. Lewis, Blackie & Son, Ltd., Glasgow, 1933.

"The Spectrochemical Analysis of Metals and Alloys," F. Twyman, Charles Griffin & Company, Ltd., London, 1941.

<div align="center">WAVE-LENGTH TABLES (SELECTED)</div>

"Wavelength Tables of 100,000 Spectrum Lines," by G. R. Harrison, John Wiley & Sons, Inc., New York, 1939.

"Wavelength Tables for Spectrum Analysis," by F. Twyman and D. M. Smith, A. Hilger, London, 1931.

"Tabelle der Hauptlinien der Linienspektra aller Elemente," by H. Kayser, Verlag J. Springer, Berlin, 1926.

"Chemical Spectroscopy," by W. R. Brode, John Wiley & Sons, Inc., New York, 1939.

"International Critical Tables," McGraw-Hill Book Company, Inc., New York.

"Handbook of Chemistry and Physics," Chemical Rubber Publishing Company.

41. Experimental.—A complete, detailed set of experiments for a course in chemical spectroscopy is given by Brode,[10] and should be consulted by the student at this point. The three simple experiments that follow are designed for three 4-hr. laboratory periods in a survey course on optical methods.

1. *The Spectroscope.*—*a.* Focus the eyepiece, telescope, and collimator as described in Sec. 16. Adjust the slit to the point

where a spectral line (mercury lamp) ceases to appear narrower and commences to become less intense. Using an arc between copper electrodes, experiment with the position of the arc and condensing lens. Place the arc about 70 or 80 cm. from the slit, and see that the image of the arc just fills the slit, with the image of the electrodes about 1 mm. above and below the slit.

b. If the instrument is equipped with a wave-length drum, check the calibration by noting the readings for several widely spaced lines in the spectrum. The lines may be identified from wave-length tables or, better, by means of a photographic chart.[69,113] The mercury arc may be used advantageously for this calibration, since its spectrum is much simpler. If the instrument is equipped with an angular degree scale, it is necessary to construct a plot of degrees vs. wave length.

c. Differentiate between rods of copper, brass, and aluminum bronze by identifying several characteristic lines in the arc spectrum.

d. Identify an unknown as Na, K, Li, Ca, or Sr by examining the flame spectrum. A Lundegardh flame or a Mitscherlich tube may be used, and the solution of the unknown should be mixed with an excess of ammonium acetate. A reagent-blank spectrum should also be observed.

2. *The Spectrograph—Qualitative Identification.—a.* If necessary, focus and adjust the instrument according to directions furnished by the maker (see Brode[10]). The alignment of source, condenser, slit, and collimator is easily checked by placing a lighted flashlight bulb in the plane of the film holder at the long wave-length side and observing its image at the end of the pointer attached to the arc stand. The focus is checked by placing a clear (fixed) photographic film or plate in the holder and examining the spectrum of a copper or iron arc by means of a magnifier. If the film is painted with an alcoholic solution of anthracene, lines in the near ultraviolet become visible by fluorescence. Adjust the slit to about 0.01 mm. and its height to about 2 mm., or use a 2-mm. mask over the film.

b. Given a sample of unknown solid material, heat a trace of it on the end of a platinum spatula in a Bunsen flame. If oxidation, combustion, or charring is observed, the sample should be oxidized with nitric acid as directed in Sec. 11. If not, it may be mixed with an equal weight of ammonium sulfate, ground in an

agate mortar, and about 2.0 mg. of the mixture placed in the crater of a graphite electrode. Powdered graphite may be added *after* grinding, if the arc fails to strike directly to the sample.

Given a sample of a solution of nitrates or sulfates saturated in $NaNO_3$ or NH_4NO_3, pipette 0.1 cc. into the heated, waterproofed craters of several graphite electrodes, $\frac{1}{4}$ in. or larger in diameter.

In either case, prepare a "blank" using all reagents except the sample.

c. Load the camera with film in total darkness. Make sure that the emulsion side is toward the prism or grating, and use great care in handling to avoid scratches or fingerprints on the emulsion. Put away the unused films, be sure that the dark slide is in the film holder, and turn on the lights. The film holder is then placed on the camera, and the dark slide is removed. Move the camera to position 1, and make a brief exposure of the copper arc spectrum, or iron arc spectrum if a very large instrument is used. Repeat at positions 5, 9, and 13. These exposures give reference lines for subsequent measurement of wave length. Use a voltage above 150 volts and a current of about 6 amp. d.c.

d. Place the "blank" electrode (anode) in the lower clamp of the arc stand, and use a pointed upper electrode. Adjust the gap to the correct position, rack the camera to position 3, and start the arc by touching the electrodes with a graphite rod. Commence the exposure at once, and expose for about 10 sec. at 6 amp. The arc is then shut off, the shutter is closed, and the crater is examined. If no material remains, add more "blank mixture" and repeat the exposure at positions 7, 11, etc. If there is a residue or if the spectrum is still strong, as evidenced by observation with a hand spectroscope, the original exposure at position 3 is continued at about 10 amp. for an additional 10 sec. The sample is replenished and the procedure is repeated at positions 7, 11, etc., with different exposure times ranging up to 1 or 2 minutes if the blank is not too volatile. A revolving sector may be used to cut down the blackening of the plate for such lengthy exposures, or the condensing lens may be stopped down or removed altogether.

e. The foregoing procedure is repeated, the sample electrode and the same upper electrode being used. Varying exposures are made at positions 2, 4, 6, 8, 10, etc., so that they are bracketed

by the reference spectra.   It is often advisable to superpose the reference spectrum on the sample spectrum.   This may, of course, be accomplished by using copper or iron supporting electrodes instead of carbon, or the reference spectrum may simply be exposed over the sample spectrum.

f. The film or plate is removed from the plateholder in total darkness and loaded into a developing tank.   If Eastman film is used, development in D11 requires 2 to 6 minutes at 70°F. with continuous agitation.   The developer is then poured off, and the short-stop solution is added.   After a few seconds, the short stop is removed and hypo is poured in.   After 2 minutes of agitation, the film may be examined.   When the backing clears, the film should be left for 2 or 3 minutes longer in the hypo, after which it should be removed, washed in a flat jet of water for 5 minutes, and dried in a current of heated air.

g. The spectral lines due to the sample are marked by placing a dot at the center of each line.   The wave lengths of several of the strongest lines are measured by the interpolation method discussed in Sec. 28.   If the spectrograph is equipped with a built-in scale printer, the wave-length measurement is simplified considerably.   The number of lines that must be measured to establish the identity of the unknown depends on the accuracy with which the measurement is made.   Thus if the precision is ± 0.001 A, only one or two lines need be measured, etc.   Note, however, the possibility of two substances giving lines of nearly the same wave length.

After measuring several wave lengths, the various possibilities for the principal constituent should be checked by observing the presence of several strong lines listed in the table.   The simplest method is to superpose the spectrum of the sample on a spectrum of the pure substance in question.   Extraneous lines are then marked with an additional dot and are identified in the same way until all lines in the spectrum are accounted for.   If an instrument of high dispersion is used, the R.U. powder spectrum is of great help in identifying lines.   It is usually possible for an experienced operator to recognize characteristic groupings of lines at a glance, and to identify the principal constituent simply by checking one or two wave lengths.

3. *The Spectrograph—Quantitative Analysis.—a.* The constituents of the sample in the foregoing experiment having been

identified, it is then necessary to determine the percentage of one minor constituent. The simple procedures given here may be used, or more elaborate and more accurate methods may be chosen (see Brode[10]).

The first step is to select a suitable homologous pair. If the principal constituent gives no suitable comparison line, then an added constituent must be used. The two lines chosen should be of about the same intensity at the concentrations employed and in the same spectral region.

b. The next step is to make up a series of standard mixtures approximating the estimated composition of the unknown. The method of Brode[11] is recommended for this step, and the details may be obtained from his book. In a short course, these graded standards should be available ready-made.

c. Two methods of estimating the composition of the sample are now possible. The first involves a visual comparison of the spectrum of the sample (plus base) with the spectra of the series of standards, in accordance with the method of Nitchie[20] (Sec. 33). Equal weights of sample and standard are arced under identical conditions for the same length of time, and the strength of the lines due to the desired constituent is compared with that of the reference substance.

An almost equally simple and far more accurate procedure involves the use of the log-sector disk (Sec. 34). Identical exposures are made for the series of standards, and the difference of the lengths of the homologous reference lines is plotted against the percentage of the desired metal. The ratio is then determined for the unknown sample, and the percentage is found directly from the graph.

The method of arcing is quite important. If relatively brief exposures are made, it is necessary to pay particular attention to the focusing of the arc image on the slit. It must not be allowed to wander, and in some cases it is necessary to use a rotating lower electrode. The crater should be refilled with sample at frequent intervals. Alternatively, Slavin[85] recommends that each sample be burned completely during a 2- or 3-minute single exposure. The illumination may be decreased by moving the arc to a considerable distance from the slit and either employing no condensing lens or else placing it immediately in front of the sector disk.

Still greater accuracy is attained through the use of the photometric method, especially in conjunction with a step sector. These methods are not quite so rapid nor so adaptable to presentation in a brief course.

PROBLEMS

1. Arrange the following metals according to the ease with which their full spectrum is excited: Fe, Cu, Zn, Na, As, Br, A.

2. What substances are responsible for the band spectra always observed in

    a. The Lundegardh flame?
    b. The carbon or graphite arc?
    c. The high-voltage spark?

3. What factors might be responsible for the nonappearance of arc spectra of the halogens? How can the halogens be excited to emit their spectra?

4. Certain lines that appear in an arc spectrum are enhanced in intensity when spark excitation is employed. Other arc lines are much weaker when excited by a spark discharge. Explain.

5. If you were to perform a qualitative spectrographic analysis of the following samples, what methods of excitation would you employ? Why? What preparation would be necessary, if any? Refer to the literature, general bibliographies, etc.

    a. Short lengths of wire about 1 mm. in diameter.
    b. Porcelain chips.
    c. Dilute solutions of metallic salts.
    d. Stain on cloth suspected of being paint.
    e. Plating on a supposedly valuable ring.
    f. Leaves of lettuce (iron, calcium, etc.).
    g. Steel rivets (phosphorus, chromium, manganese, etc.).
    h. Powdered ore.
    i. Lead in tap water.
    j. Manganese in muscle tissue.
    k. Platinum and iridium in jewelry.
    l. Analytical precipitate on filter paper.

6. Draw up a table showing the scope, optimum use, advantages, and disadvantages of the several methods of exciting spectra.

7. What are the functions of a flux or base mixture? Why is ammonium sulfate generally used?

8. Bearing in mind the factors affecting theoretical dispersion, list other factors that will affect the linear dispersion of a prism spectrograph.

9. What factors affect the actual observed resolving power of a grating spectrograph? Of a prism spectrograph?

10. Why should the focal plane of a prism spectrograph lie along a line at an angle to the optical axis, instead of normal to it? Sketch.

11. The focal length of a collimating lens is 50 cm. and its effective diameter is 5 cm.   What is the theoretical slit width at 5,890 A?   What is the optimum slit width?

12. What is the resolving power at 5,000 A of a 30,000 lines per inch concave grating whose radius of curvature is 106 cm. if the width of the grating is 7 cm.?   What is the theoretical resolving power for the second-order spectrum?

13. What factors govern the dispersion of a concave grating?

14. It is often observed that particles of dust or minute irregularities on the jaws of the slit of a concave grating spectrograph are not imaged in the spectrum.   What might be responsible for this?

15. What disadvantages are inherent in spectrographs of high dispersion? Of low dispersion?   What is the principal advantage of the latter?

16. Assume that you are confronted by the responsibility of recommending the purchase of a certain type of spectrograph for precise routine quantitative and qualitative analyses on ferrous die castings.   What type of instrument would you recommend?   Back your decision by adequate reasons and authoritative statements from the literature.

17. The Littrow spectrograph is sometimes fitted with three interchangeable dispersing systems.   What are they, and for what ranges are they used?

18. What would you consider to be the major source of error in the quantitative method of Nitchie?   Could this be remedied by using a photometer or log-sector disk?

19. Perform calculations for the log-sector and photometer methods, using data furnished by the instructor.

REFERENCES

1. G. KIRCHOFF and R. BUNSEN, *Pogg. Ann.*, **110**, 161 (1860).
2. A. DEGRAMONT, *Compt. rend.*, series of papers (1900).
3. W. N. HARTLEY, *Phil. Trans. London*, **175**, 326 (1884).
4. W. F. MEGGERS and B. F. SCRIBNER, "Index to the Literature on Spectrochemical Analysis for 1920–1937," A.S.T.M., Philadelphia, 1939.
5. R. A. SAWYER and H. B. VINCENT, "Proceedings of the Seventh Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1940.
6. H. W. THOMPSON, "A Course in Chemical Spectroscopy," Oxford, Clarendon Press, New York, 1934.
7. H. E. WHITE, "Introduction to Atomic Spectra," McGraw-Hill Book Company, Inc., New York, 1934.
8. F. K. RICHTMYER and E. H. KENNARD, "Introduction to Modern Physics," McGraw-Hill Book Company, Inc., New York, 1942.
9. S. GLASSTONE, "Textbook of Physical Chemistry," D. Van Nostrand Company, Inc., New York, 1940.
10. W. R. BRODE, "Chemical Spectroscopy," John Wiley & Sons, Inc., New York, 1939.
11. S. J. LEWIS, "Spectroscopy in Science and Industry," Blackie & Sons, Ltd., Glasgow, 1933.

12. P. L. Hibbard, *Ind. Eng. Chem. Anal. Ed.*, **10**, 615 (1938).

13. E. Bayle and L. Amy, *Ann. méd. légale criminol. police sci.*, **8** (1928); *Compt. rend.*, **185**, 268 (1927).

14. F. Rohner, *Helvetica Chim. Acta*, **21**, 23 (1938).

15. A. E. Ruehle and E. K. Jaycox, *Ind. Eng. Chem. Anal. Ed.*, **12, 260** (1940).

16. T. M. Hess, J. S. Owens, and L. G. Reinhardt, "Proceedings of the Seventh Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1940; *Ind. Eng. Chem. Anal. Ed.*, **11**, 646 (1939).

17. H. G. Lundegardh, "Die Quantitative Spektralanalyse der Elemente," Gustav Fischer, Jena, 1929–1934.

18. A. E. Ruehle and E. K. Jaycox, "Proceedings of the Seventh Summer Conference on Spectroscopy and Its Applications," p. 10, John Wiley & Sons, Inc., New York, 1940.

19. D. T. Ewing, M. F. Wilson, and R. P. Hibbard, *Ind. Eng. Chem. Anal. Ed.*, **9**, 410 (1937).

20. C. C. Nitchie, *ibid.*, **1**, 1 (1929).

21. M. A. Griggs, R. Johnstin, and B. E. Elledge, *ibid.*, **13, 99** (1941).

22. H. W. Lohse, *Can. J. Research*, **12**, 519 (1935).

23. H. Ramage, *Nature*, **123** (1929).

24. R. A. Sawyer and H. B. Vincent, "Proceedings of the Sixth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1939.

25. J. Schuch, "Proceedings of the Seventh Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1940.

26. A. T. Myers and B. C. Brunstetter, *Ind. Eng. Chem. Anal. Ed.*, **11**, 218 (1939).

27. W. Gerlach and W. Gerlach, "Clinical and Pathological Applications of Spectrum Analysis," A. Hilger, London, 1934.

28. J. S. Owens, *Metals and Alloys*, **9,** 15 (1938).

29. A. H. Staud and A. E. Ruehle, *Ind. Eng. Chem. Anal. Ed.*, **10,** 59 (1938).

30. G. W. Standen and L. Kovach, *Proc. Am. Soc. Testing Materials*, **35 II,** 79 (1935).

31. L. J. Lewis, "Spectroscopy in Science and Industry," Blackie & Son, Ltd., Glasgow, 1933.

32. H. W. Brownsdon and E. H. S. vÂn Someren, *J. Inst. Metals*, 46 (1931).

33. S. S. Ballard and P. L. Gow, *J. Applied Phys.*, **10**, 556 (1939).

34. E. Bayle and L. Amy, *Compt. rend.*, **185**, 268 (1927).

35. M. F. Hasler, *J. Optical Soc. Am.*, **31**, 140 (1941).

36. E. C. C. Baly, "Spectroscopy," Longmans, Green & Company, New York, 1927–1929.

37. L. W. Strock, "Spectrum Analysis with the Carbon Arc Cathode Layer," A. Hilger, London, 1936.

38. N. K. CHANEY, V. C. HAMISTER, and S. W. GLASS, *Trans. Electrochem. Soc.*, **67** (1935).
39. M. F. HASLER, "Proceedings of the Fifth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1938.
40. O. S. DUFFENDACK and R. A. WOLFE, *ibid.*
41. O. S. DUFFENDACK, R. A. WOLFE, and R. W. SMITH. *Ind. Eng. Chem. Anal. Ed.*, **5**, 226 (1933).
42. K. PFEILSTICKER, *Z. Elektrochem.*, **43**, 719 (1937).
43. H. KAISER, "Proceedings of the Seventh Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1940.
44. F. TWYMAN and C. S. HITCHEN, *Proc. Roy. Soc. (London)* A, **133**, 72 (1931).
45. O. FEUSSNER, *Z. tech. Physik.*, **13**, 573 (1932).
46. R. HULTGREN, *J. Am. Chem. Soc.*, **54**, 2320 (1932).
47. F. W. LAMB, *Ind. Eng. Chem. Anal. Ed.*, **13**, 185 (1941).
48. R. J. KEIRS and D. T. ENGLIS, *ibid.*, **12**, 275 (1940).
49. A. SCHUSTER, *Z. Physik*, **65**, 547 (1930); *Astrophys. J.*, **21**, 197 (1905).
50. J. REILLY and W. N. RAE, "Physico-chemical Methods," Methuen & Co., Ltd., London, 1940.
51. D. C. STOCKBARGER and L. BURNS, *J. Optical Soc. Am.*, **23**, 379 (1933).
52. S. S. BALLARD and P. L. GOW, *J. Applied Phys.*, **10**, 556 (1939).
53. F. H. EMERY, *J. Optical Soc. Am.*, **31**, 160 (1941).
54. B. H. CARROLL, "Proceedings of the Sixth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1939.
55. C. E. K. MEES, *J. Optical Soc. Am.*, **25**, 80 (1935).
56. B. KRAEMER, *Z. Elektrochem.*, **38**, 51 (1932); **37**, 862 (1931).
57. R. W. WOOD, "Physical Optics," The MacMillan Company, New York, 1934.
58. G. H. DIEKE, "Proceedings of the Sixth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1939; *J. Optical Soc. Am.*, **23**, 274 (1933).
59. W. F. MEGGERS, *J. Applied Phys.*, **10**, 734 (1939).
60. E. S. MILLER, "Quantitative Biological Spectroscopy," Burgess Publishing Co., Minneapolis, 1939.
61. R. A. SAWYER and H. B. VINCENT, *J. Optical Soc. Am.*, **31**, 47 (1941).
62. G. R. HARRISON, "Proceedings of the Seventh Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1940.
63. W. S. BAIRD, "Proceedings of the Sixth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1939.
64. A. PORITSKY, "Proceedings of the Fifth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1938.

65. W. F. MEGGERS and K. BURNS, *Bur. Standards Sci. Tech. Papers*, **18,** 185 (1922).

66. J. H. DOWELL, *J. Sci. Instruments*, **18,** 208 (1940).

67. G. R. HARRISON, "Proceedings of the Fifth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1938.

68. M. SLAVIN, "Proceedings of the Seventh Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1940.

69. "A Spectrogram of Copper," A. Hilger, London.

70. Technical Publications of A. Hilger, London.

71. R. A. SAWYER and H. B. VINCENT, *Spectro. Chim. Acta.*, **1,** 131 (1939).

72. F. TWYMAN and D. M. SMITH, "Wave Length Tables for Spectrum Analysis," A. Hilger, London, 1931.

73. J. BARDET, "Atlas de spectres d'arc," Gaston Dorn et Cie., Paris, 1926

74. "Arc Spectrum of the R.U. Powder," A. Hilger, London.

75. W. C. PIERCE, O. TORRES, and W. W. MARSHALL, *Ind. Eng. Chem. Anal. Ed.*, **11,** 191 (1939).

76. "Copper Arc Spectrum," A. Hilger, London.

77. W. J. CROOK, "Metallurgical Spectrum Analysis," Stanford University Press, Stanford University, Calif., 1935.

78. C. H. EDLIN, *J. Sci. Instruments*, **11,** 357 (1934).

79. W. F. MEGGERS, "Proceedings of the Seventh Summer Conference on Spectroscopy and Its Applications," p. 73, John Wiley & Sons, Inc., New York, 1940.

80. F. TWYMAN and F. SIMEON, *Trans. Optical Soc. (London)*, **31,** 179 (1929–1930).

81. E. SCHWEITZER, *Z. anorg. allgem. Chem.*, **164,** 127 (1927); **165,** 364 (1927).

82. W. GERLACH, *ibid.*, **142,** 383 (1925).

83. W. R. BRODE, "Proceedings of the Sixth Summer Conference on Spectroscopy and Its Applications," 1939; "Proceedings of the Seventh Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1940; *J. Optical Soc. Am.*, **31,** 58 (1941).

84. V. K. PROKOF'EV, *Bull. Acad. Sci. U.S.S.R.*, **4,** 5 (1940).

85. M. SLAVIN, *Ind. Eng. Chem. Anal. Ed.*, **10,** 407 (1938).

86. E. PREUSS, *Chem. Erde*, **9,** 365 (1935).

87. W. GERLACH and E. SCHWEITZER, "Foundations and Methods of Chemical Analysis by the Emission Spectrum," A. Hilger, London, 1930.

88. W. GERLACH and W. RIEDL, "Die chemische Emissionsspektralanalyse," Vol. III, Voss, Leipzig, 1936.

89. F. TWYMAN, *Trans. Optical Soc. (London)*, **33** (1931–1932).

90. G. SCHEIBE, *Z. angew. Chem.*, **42,** 1017 (1929).

91. D. M. SMITH, *Brit. Non-ferrous Metals Research Assoc.* monograph, London, 1933.

92. F. TWYMAN and A. HARVEY, *J. Iron Steel Inst. (London)*, **2,** 397 (1932).

93. B. O'BRIEN, "Proceedings of the Sixth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1939.

94. D. H. FOLLETT, *J. Sci. Instruments*, **13**, 221 (1932).

95. H. A. WILHELM, *Ind. Eng. Chem. Anal. Ed.*, **9**, 170 (1937).

96. L. W. STROCK, *Spectro. Chim. Acta.*, **1**, 123 (1929).

97. B. F. SCRIBNER, "Proceedings of the Fifth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1938.

98. G. R. HARRISON, *J. Optical Soc. Am.*, **24**, 59 (1934).

99. D. M. SMITH, *Brit. Non-ferrous Metals Research Assoc.*, RRA524, (November, 1939).

100. E. M. THORNDIKE, *Ind. Eng. Chem. Anal. Ed.*, **13**, 66 (1941).

101. L. A. WOODWARD and R. G. HORNER, *J. Sci. Instruments*, **12**, 17 (1935).

102. P. H. BELL, *Ind. Eng. Chem. Anal. Ed.*, **10**, 579 (1938).

103. K. B. THOMSON and O. S. DUFFENDACK, *J. Optical Soc. Am.*, **23**, 101 (1933).

104. R. A. WOLFE, *Proc. Am. Soc. Testing Materials*, II, **35**, 87 (1935).

105. J. S. OWENS, "Proceedings of the Fifth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1938.

106. R. BRECKPORT and L. LIALINE, *Ann. soc. sci. Bruxelles*, **55**, 30 (1935).

107. J. S. FOSTER, G. O. LANGSTROTH, and D. R. MCRAE, *Proc. Roy. Soc. (London) A*, **153**, 141 (1935).

108. "Bulletin of Spectrum Analysis," A. Hilger, London, March, 1929.

109. H. TRICHÉ, *Rev. optique*, **16**, 161 (1937).

110. M. F. HASLER and R. W. LINDHURST, *Rev. Sci. Instruments*, **7**, 137 (1936).

111. G. SCHEIBE and O. SCHNETTLER, *Naturwissenschaften*, **19**, 134 (1931).

112. A. WENDT and H. HEUN, *Z. Physik*, **93**, 92 (1934).

113. W. SEITH and K. RUTHARDT, "Chemische Spektralanalyse," Verlag J. Springer, Berlin, 1938.

114. W. SEITH and E. HOFER, *Z. Elektrochem.*, **40**, 313 (1934).

CHAPTER II

THE SPECTROPHOTOMETER

42. Before discussing the topics included in this chapter, it may be wise to point out that they are treated only from the viewpoint of the analytical chemist and that, owing to the limited scope of this book, it is necessary to omit many interesting and important aspects. It is not possible, for instance, to discuss the use of absorption spectra in elucidating molecular structure, nor is it considered advisable to give more than passing mention to the field of color analysis and specification, even though the latter is of importance in paint and textile chemistry, etc.[1,2]

The analytical chemist is primarily concerned with the measurement of color only in so far as it is useful in qualitative or quantitative chemical analysis, and the treatment of the subject given here is therefore restricted to this field. The applications of colorimetry and spectrophotometry to chemical analysis are, however, exceedingly numerous. Attention should be called to two of the standard texts on chemical colorimetry, that by Yoe[3] and that by Snell and Snell.[4] Brode[5] gives an excellent résumé of photometric methods, and there are several Hilger publications on spectrophotometry.[6,7,11] Biological applications are described by E. S. Miller.[9] The bibliography by Walker[8] is especially good.

Briefly, the spectrophotometric method is applicable in general to the following types of problem:

1. Quantitative analysis for certain cations, anions, and organic groups in concentrations ranging from a few thousandths of a per cent in 1 or 2 cc.

2. Vitamin assay and qualitative and quantitative analysis of certain complex organic molecules.

3. Measurement of pH, dissociation, reaction rate, etc.

4. Investigation of molecular structures.

5. Preliminary to colorimetric analysis and analysis of mixtures.

This list will be elaborated in subsequent sections, but the student should examine some of the preceding references in

order to get an idea of the enormous number and the great diversity of the available procedures.

43. Production of Color by Absorption.—A medium is said to be colored if it absorbs light whose wave length lies somewhere within the visible range of the spectrum. The color of the medium obviously will be complementary to the color absorbed; *e.g.*, a pure blue solution will transmit blue light and absorb light of other wave lengths (see Table 6). If white light is passed through such a solution and the transmitted light is viewed through a spectroscope, the spectrum may have the appearance of Fig. 55*a*.

In order to provide a logical basis for measuring the absorption of light, it is necessary to allow for losses by reflection and scattering at the boundaries of the cell containing the medium and also for the small losses caused by scattering within the liquid itself. This correction is made by comparing the intensity I of a ray that has passed through the colored medium with the intensity I_o of the same ray after passage through a colorless medium of similar refractive index contained in an identical cell.

TABLE 6

Wave length, mμ	Hue (transmitted)	Complementary hue
400–435	Violet	Yellowish green
435–480	Blue	Yellow
480–490	Greenish blue	Orange
490–500	Bluish green	Red
500–560	Green	Purple
560–580	Yellowish green	Violet
580–595	Yellow	Blue
595–610	Orange	Greenish blue
610–750	Red	Bluish green

The ratio $I/I_o \times 100$ is then the percentage transmission of the sample.

The color of a given medium is easily expressed in the form of a graph of percentage transmission vs. wave length as shown in Fig. 55*b*. The shape of such a curve is more or less characteristic of the absorbing substance, but it also depends on several other factors such as the thickness of the cell, the concentration of the colored substance, if a solution, and the chemical nature of the solvent and solution.

Some media will give smooth transmission curves without well-marked points of inflection (Fig. 56), whereas others will show maxima or minima (Fig. 57).   The former property is termed *general absorption*, and the latter, which is more common, is called *selective absorption*.   All substances exhibit absorption in some
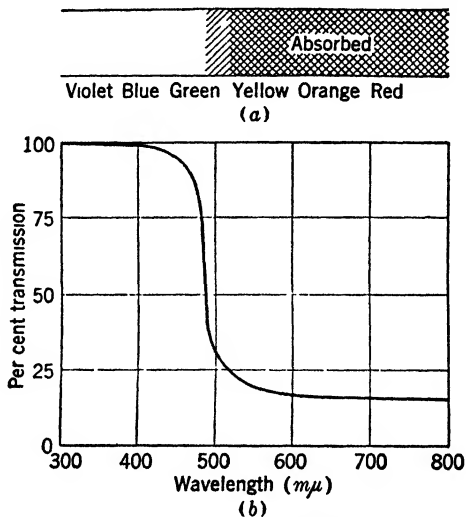

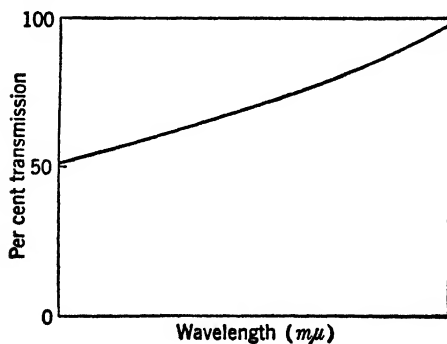Fig. 55.—Graphical recording of absorption

Fig. 56.—General absorption.

region of the electromagnetic spectrum.   For example, colorless benzene gives a complicated group of maxima and minima in the ultraviolet region (Fig. 58), whereas water shows strong absorption in the near infrared.   These extensive invisible regions of the spectrum may be investigated photographically or by other

means and are even more significant in some fields of analytical chemistry than the visible region itself.

44. The Beer-Lambert Law—Symbols and Calculations.— When a ray of monochromatic light enters an absorbing medium,
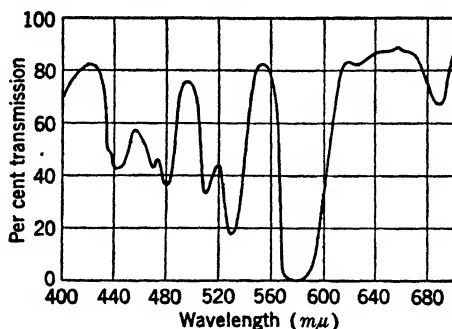

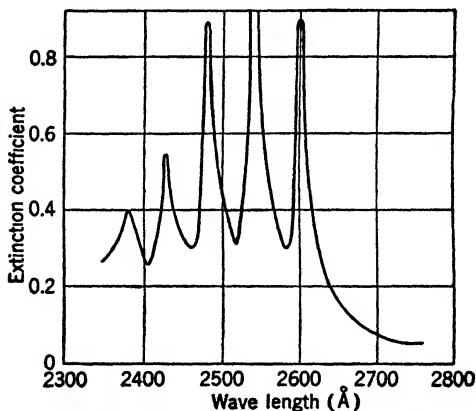Fig. 57.—Selective absorption—an extreme example. (Didymium glass.)

Fig. 58.—Absorption curve of benzene.

its intensity decreases exponentially in accordance with the equation of Lambert

$$I = I_o e^{-\mu l}$$

which is more conveniently expressed as

$$\log_{10}\left(\frac{I_o}{I}\right) = Kl$$

where K is a constant for any given wave length, l is the thickness of the absorbing medium, and I_o and I refer to the original and

transmitted intensities, respectively, at a given wave length, after correction for losses by reflection, etc., as mentioned in the preceding section.

If the absorbing medium is a solution, the foregoing law still applies, but the concentration of the colored solute must also be taken into account. As might be expected, the absorption shown by a given thickness of solution is dependent on the number of colored solute molecules traversed by the ray of light. Since the number of colored molecules traversed is dependent on the concentration of solute and since the transmitted intensity varies logarithmically with the thickness of the column of liquid, Lambert's law may be expressed as

$$\log_{10}\left(\frac{I_o}{I}\right) = kcl$$

where c is the concentration of colored solute. This equation is usually referred to as the Beer-Lambert law[10] or as the Bouger-Beer law.

For a pure liquid, the solute concentration c equals unity and the expression becomes equivalent to Lambert's law. Notice that the actual value of the intensity does not enter into any of the equations given. Only the relative value (I_o/I) is significant.

The Beer-Lambert law is found to apply in all cases where no alteration of the solute molecules has occurred. If the solute molecules dissociate, ionize, or associate, this law does not necessarily hold, and it is possible to calculate the extent of the dissociation, etc., from the observed discrepancies. As one would expect, *the law applies in a strict sense only for monochromatic light.*

In practice, certain usages have become conventional in respect to the terms and units involved in the Beer-Lambert calculations, but some confusion exists concerning the symbols employed. The list given in Table 7 presents a few of the commonly encountered symbols and their definitions. When referring to the literature, however, it is always advisable to check the units employed by the author.

The quantity $E_1^{1\%}$ is particularly useful when the molecular weight of the solute is unknown.

Certain conventions are also observed regarding the method of plotting absorption curves. The common procedure is to plot

TABLE 7.—DEFINITIONS OF TERMS

A = absorption = $1 - T$.

c = concentration, g./liter, or mg./cc.

d = density = $\log_{10}(I_o/I)$.

E = extinction = d = $\log_{10}(I_o/I)$.

$E_{1\,cm}^{1\%}$ defined by $\log_{10}(I_o/I) = E_{1\,cm}^{1\%}\ pl$.

e = base of natural logarithms = 2.7183.

I_o and I = intensity transmitted by solvent and solute, respectively

k = specific extinction $\log_{10}(I_o/I) = kcl$.

k' = absorption index $I = I_o e^{-(4\pi k' l/\lambda)} = 0.183c\lambda\epsilon$.

K = extinction coefficient $\log_{10}(I_o/I) = Kl$.

l = length of column of absorbing material, cm.

M = molecular weight.

p = percentage of solute (grams per 100 g).

r = absorption ratio = $E_{\lambda_1}/E_{\lambda_2}$ where λ_1 and λ_2 are any specified wave lengths.

T = transmission = (I/I_o).

$\% T$ = percentage transmission = $100\ T$.

α = specific absorption coefficient $I = I_o \cdot \alpha^{-cl}$.

ϵ = molecular extinction = Mk.

μ = absorption coefficient $I = I_o e^{-\mu l}$.

$$\log_{10}\left(\frac{I_o}{I}\right) = kcl = \frac{\epsilon cl}{M} = E_{1\,cm}^{1\%}\ pl = d = E.$$

the percentage of transmission vs. wave length in millimicrons, as shown in Fig. 59a. A recommended method is to plot increasing values of E, $\log E$, or ϵ vs. increasing values of frequency in Fresnel units $[f = (3 \times 10^5)/\lambda$ (in mμ)$]$ or decreasing values of wave length in millimicrons (Fig. 59b, c).   The use of extinction instead of percentage transmission as the ordinate increases the sharpness of the maxima and makes high absorption values more significant.

A simplification of the Beer-Lambert law may be derived as follows: Consider two solutions of different concentrations of the same solute contained in two cells and illuminated by the same source.   Then the transmissions of these solutions will be

$$\log\left(\frac{I_o}{I_1}\right) = kc_1 l_1$$

and

$$\log\left(\frac{I_o}{I_2}\right) = kc_2 l_2$$

If we alter the thickness of one cell or the other until the two

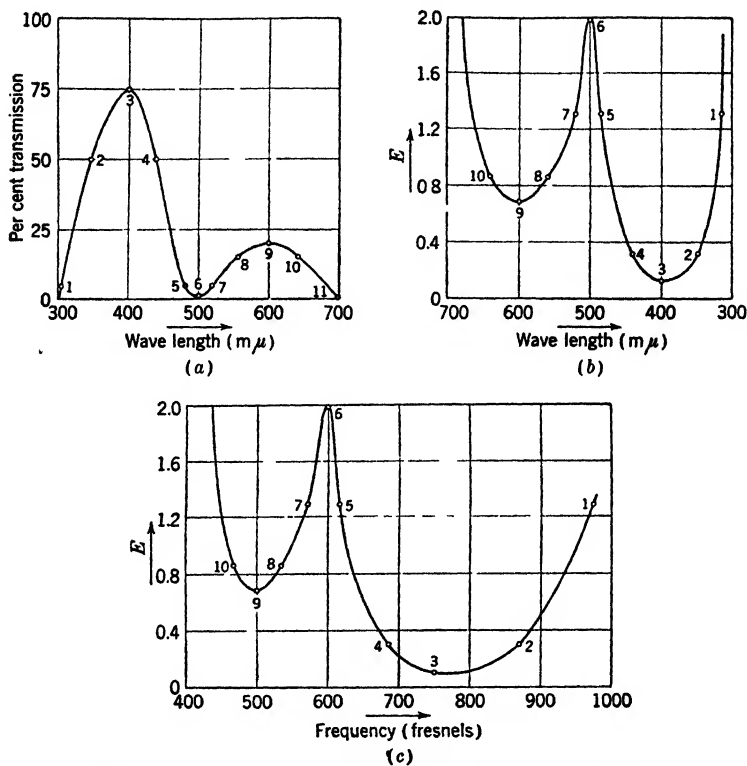solutions transmit the same intensity, then

$$I_1 = I_2$$

Fig. 59.—Effect of the method of plotting on the shape of the absorption curve.

On dividing the two equations, we obtain the simple proportion (also known as Beer's law)

$$c_1 l_1 = c_2 l_2$$

or

$$c_1 : c_2 = l_2 : l_1$$

These proportions will be referred to again in Sec. 69, for they are the fundamental equations on which the use of the balancing colorimeter depends.

45. The factors affecting absorption may be placed in two groups: inherent effects and instrumental effects. The latter will be discussed under the appropriate heading (Sec. 50), but

the inherent factors may be considered properly at this time. Among these, we may include the effects of concentration, the chemical nature of the solvent and solution, and temperature.
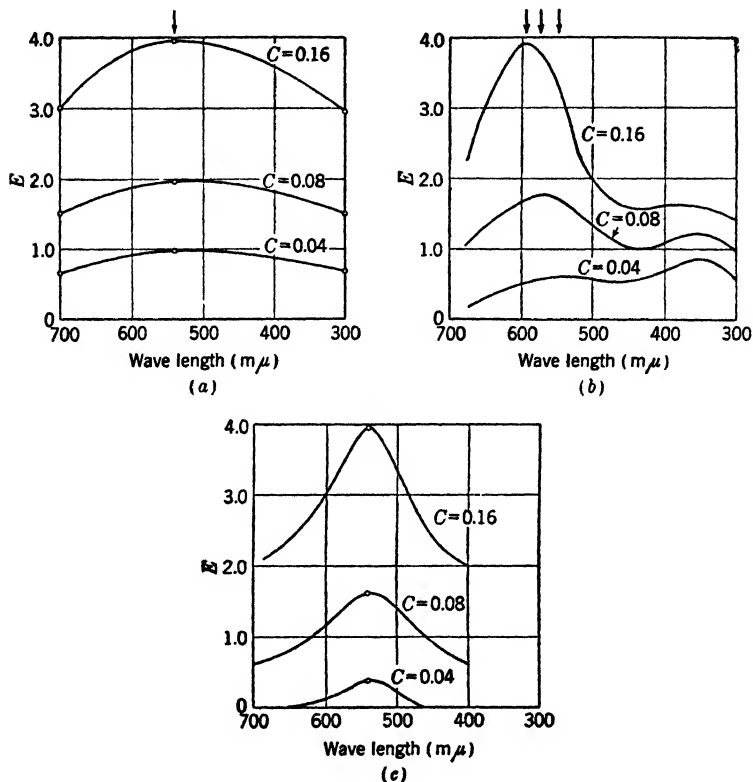

Fig. 60.—Relation of absorption curve to Beer's law: (a) Beer's law followed; (b) shift in position of maximum and consequent failure of Beer's law at 610 mμ; (c) no shift in position of maximum, but E not proportional to concentration.

It follows from the preceding paragraph that Beer's law is followed when at any given wave length it is found that

$$c_1 : c_2 = l_2 : l_1$$

or when k of the expression $\log_{10}(I_o/I) = kcl$ is in fact a constant (Fig. 60a). Deviations from these conditions with resultant failure of Beer's law may occur either as a result of a shift in the shape of a given portion of the transmission curve as the concentration changes (Fig. 60b), or because of the absence of a logarithmic relation between concentration and transmission. It is

obvious that Fig. 60b indicates some form of chemical transformation in which a second colored component is involved, as for instance the conversion of one colored form of an indicator into a second colored form. The phenomenon illustrated in Fig. 60c is capable of several interpretations, among them the change of part of the colored substance into a colorless form, *e.g.*, the dissociation of a colorless substance to give colored ions, or vice versa. Ionization, association, solvation, dissociation, tautomerism, etc., may give rise to such effects, and it is easy to see that spectrophotometric observations might be of use in studying these phenomena. The chemical nature of both solute and solvent will obviously determine the occurrence and extent of these deviations, with special reference to the polar or nonpolar properties. A familiar extreme example is the change in color of iodine solutions with the nature of the solvent. Iodine in nonpolar carbon tetrachloride is deep purple, whereas the color of an alcoholic solution is brown. It is significant that the presence of only 1 per cent alcohol is sufficient to change the color and hence the shape of the transmission curve of iodine in carbon tetrachloride. For this reason, the absolute purity of the solvent is of great importance in spectrophotometric work, especially in the ultraviolet region.

Twyman and Alsopp[11] give directions for purifying the common solvents. Their procedure is improved by substituting fractional distillation for the simple distillation that they recommend. A 10- or 12-plate still may be used to advantage.

The solvent must, of course, show no absorption bands in the spectral region to be investigated and must be capable of ready purification. Water, alcohol, and most colorless solvents are suitable for the visual range, but especially purified ethyl ether, ethylacetate, cyclohexane, or 2,2,4-trimethylpentane (iso-octane) are generally used for ultraviolet measurements.

Brode[5] gives the transmission limits of a variety of solvents and indicates the advantages of inert nonpolar solvents such as aliphatic hydrocarbons. Hogness[12] claims that iso-octane is a superior solvent for ultraviolet work because of the ease with which it may be purified.

The effect of ordinary fluctuations in room temperature is not usually serious in analytical spectrophotometry, and no general rule may be given concerning its effect on absorption. Precise

work is customarily carried out in a constant-temperature room. The temperature coefficient of transmission is sometimes defined as

$$E_t = E_{25°} + \delta l \frac{(t - 25)}{15}$$

where E_t and $E_{25°}$ refer to extinction values measured at $t°$ and 25°C., respectively. δ is the temperature coefficient.

One factor that may cause considerable annoyance is the tendency of certain materials to bleach or discolor when exposed to light. Such photochemical reactions are most apt to occur when the sample is stored in a warm, brightly lighted room, but in some cases photochemical decomposition takes place during the process of spectrophotometric observation, especially in the ultraviolet region. The intensity of illumination in most spectrophotometers, however, is below the danger level, but the possible occurrence of the effect should nevertheless be borne in mind.

SPECTROPHOTOMETERS

46. The instruments that are used to measure transmission at various wave lengths are called spectrophotometers. Such instruments are to be distinguished from filter photometers and colorimeters (Chap. III), which permit measurements at only a few wave lengths.

The essential features of any spectrophotometer are: a dispersing system, an optical train which includes a cell containing the colored sample and a second cell containing the reference substance, and a device for comparing the intensities transmitted by the colored sample and reference substance. Spectrophotometers may be classified according to the method used to accomplish these three objectives, especially the method of comparing intensities. In the following paragraphs, the discussion of the instruments is arranged according to whether the transmission is measured visually, by photoelectric means, or photographically.

47. Visual Instruments.—A typical visual spectrophotometer (Hilger-Nutting) is shown schematically in Fig. 61. Light from source S is divided into two beams by prisms P. These beams then pass through two identical cells C_1 and C_2, containing solvent and solution, respectively. After passing through the polarizing prisms N_1 and N_2, the beams are made adjacent by

rhomb R whose edge forms the dividing line between them. The adjacent beams pass through the polarizing prism N_3 and are focused on the slit of the spectroscope D by the lens L_2. The polarizing prism N_3 is mounted in a rotating scale S_C graduated both in degrees and in density units corresponding to $\log (I_o/I)$. After suitable adjustment of prisms N_1 and N_2 when both cells contain solvent only, the adjacent spectra viewed through the spectroscope will be matched in brilliance when the scale S reads zero density. If the colored solution is then placed in cell C_2, the brilliance of the solution spectrum will be reduced
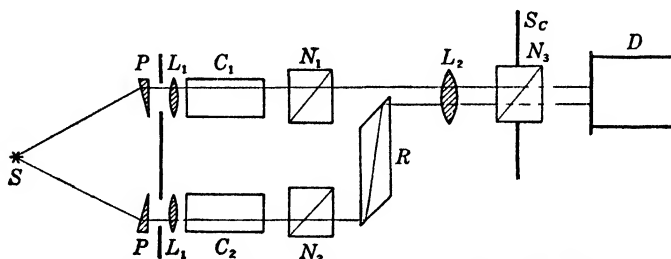
Fig. 61.—Visual spectrophotometer (schematic).   (*After Hilger-Barfit-Nutting Photometer.*)

S = source
P = collimating prism
L_1 = condenser to render rays parallel
C_1 = cell containing solvent
C_2 = cell containing solution
N_1, N_2 = polarizing prisms
R = totally reflecting rhomb
N_3 = polarizing prism in rotating mount
S_c = graduated circular scale
D = slit and collimating tube of constant deviation spectroscope

in those regions of the spectrum where absorption occurs. The two spectra may again be matched in brilliance at some wave length by rotating prism N_3, and the density $\log (I_o/I)$ may be determined at the particular wave-length setting by reading the scale Sc. An accuracy of about ± 1 per cent is claimed for this instrument, but the accuracy is considerably decreased near the ends of the spectrum where the eye is less sensitive (see E Fig. 69).

The two polarizing prisms N_1 and N_2 may be advantageously replaced by the so-called Wollaston polarizer shown in Fig. 62. This prism is used in most visual spectrophotometers and in many of the photoelectric types. Its principle is illustrated in Figs. 63 and 64.

The Bausch and Lomb instrument, shown in Fig 63 employs the Wollaston prism, and although similar to the instrument just mentioned, it has the added advantage that the thickness of the cells may be altered at will, thus permitting the study of both dark and light solutions
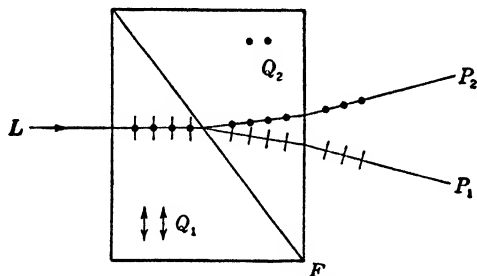

FIG 62 — The Wollaston polarizer

I = ray of unpolarized light
Q_1 and Q_2 = quartz prisms whose optic axis directions are indicated by $\updownarrow$ and ●
P_1 = polarized ray vibrating in plane of drawing
P = polarized ray vibrating in plane normal to drawing
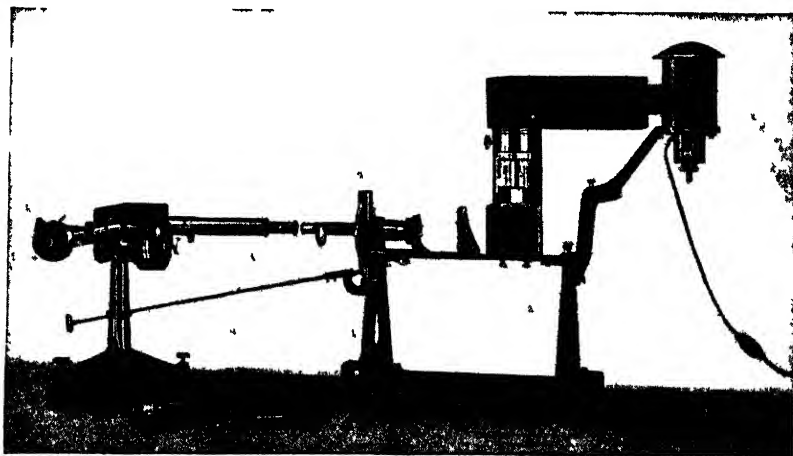
FIG 63a

A more compact laboratory instrument is the Koenig-Martens spectrophotometer made by Schmidt and Haensch   The diagram shown in Fig 64 is more or less self-explanatory in the light of the preceding explanations, since the principles are similar.   The Weigert instrument shown in Fig. 65 and a
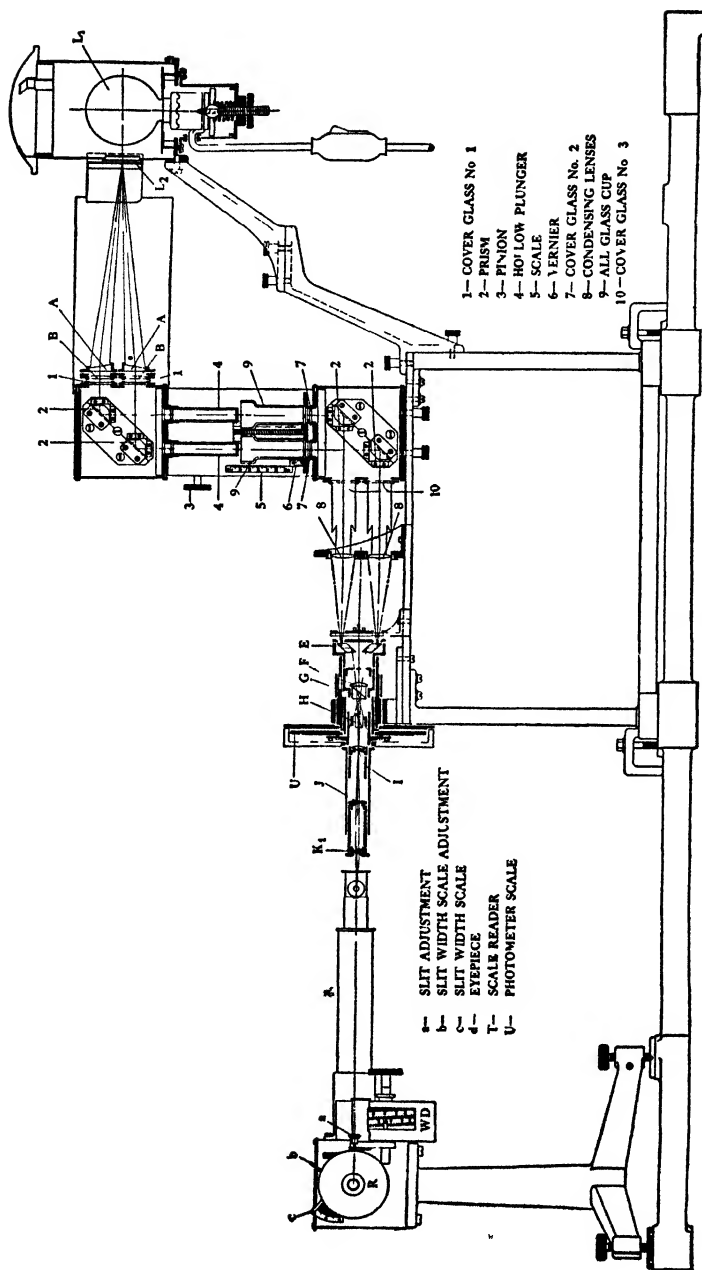
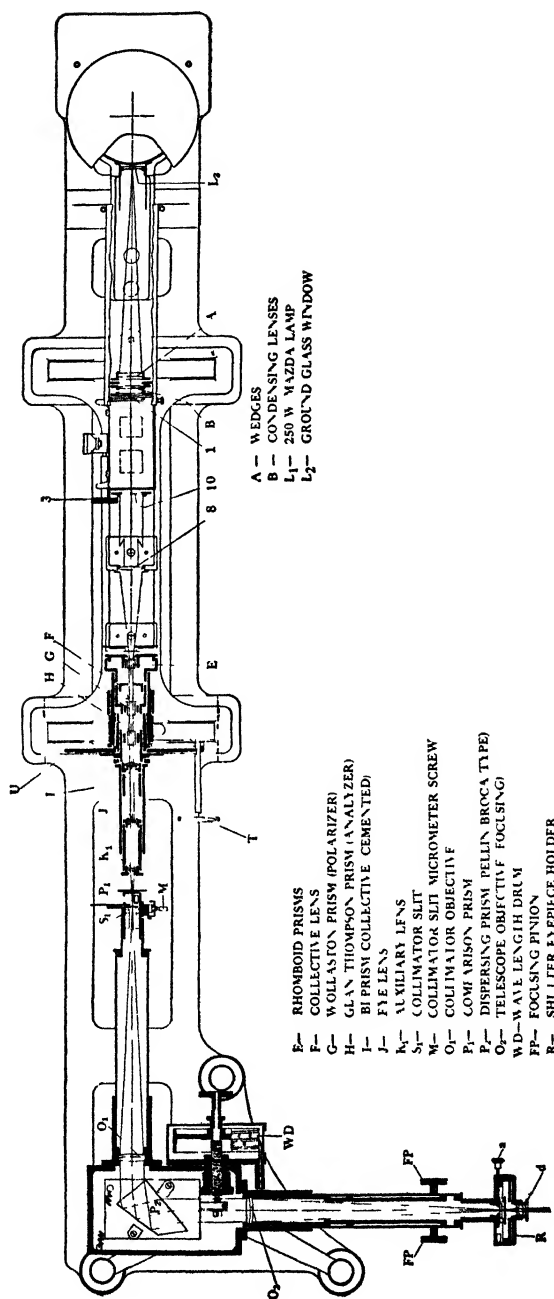1—COVER GLASS No. 1
2—PRISM
3—PINION
4—HOT LOW PLUNGER
5—SCALE
6—VERNIER
7—COVER GLASS No. 2
8—CONDENSING LENSES
9—ALL GLASS CUP
10—COVER GLASS No. 3

↓ SLIT ADJUSTMENT
↓ SLIT WIDTH SCALE ADJUSTMENT
↓ SLIT WIDTH SCALE
↓ EYEPIECE
T— SCALE READER
U— PHOTOMETER SCALE

Fig. 63b.

A — WEDGES
B — CONDENSING LENSES
L_1— 250 W MAZDA LAMP
L_2— GROUND GLASS WINDOW

E— RHOMBOID PRISMS
F— COLLECTIVE LENS
G— WOLLASTON PRISM (POLARIZER)
H— GLAN THOMPSON PRISM (ANALYZER)
I— BI PRISM COLLECTIVE CEMENTED)
J— EYE LENS
k_1— AUXILIARY LENS
S_1— COLLIMATOR SLIT
M— COLLIMATOR SLIT MICROMETER SCREW
O_1— COLLIMATOR OBJECTIVE
P_1— COMPARISON PRISM
P_2— DISPERSING PRISM (PELLIN BROCA TYPE)
O_2— TELESCOPE OBJECTIVE FOCUSING)
WD— WAVE LENGTH DRUM
FP— FOCUSING PINION
R— SHUTTER EYEPIECE HOLDER

Fig. 63c.—The Bausch and Lomb spectrophotometer.   (Courtesy of Bausch & Lomb Optical Company.)

similar instrument employing a Hufner rhomb depend on a revolving adjustable sector for diminishing the intensity of the ray that passes through the solvent. Other instruments are described by Walsh[11] and Böttger.[15]

Ashley,[13] who gives a comprehensive discussion of the errors and limitations of visual and photoelectric instruments, points out that since $\log (I_o/I) = kcl = Kl$, then $K = kc$ and $dK/dc = k$.
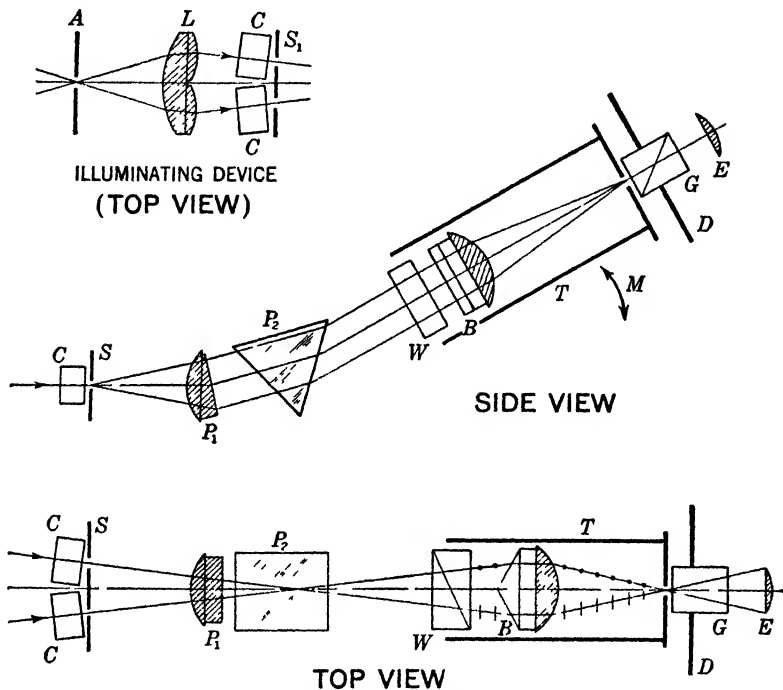
FIG. 64. —The Koenig-Martens spectrophotometer (schematic)

From this expression, it follows that the change in extinction coefficient per given change in concentration will be largest when the specific extinction is large, i.e., when the transmission of a solution is small. In other words, the theoretical sensitivity dK/dc of the spectrophotometric method is at a maximum when the transmitted intensity is low. Since the eye is least sensitive to changes in small intensities, the two factors counterbalance one another. Ashley states that the accuracy of visual measurements of E is about ± 0.01, whereas photoelectric methods may be considerably more accurate.

Although a more complete discussion of the factors affecting the accuracy of spectrophotometers will be given in Secs. 52 and 53, it should by clearly stated here that all reported measurements
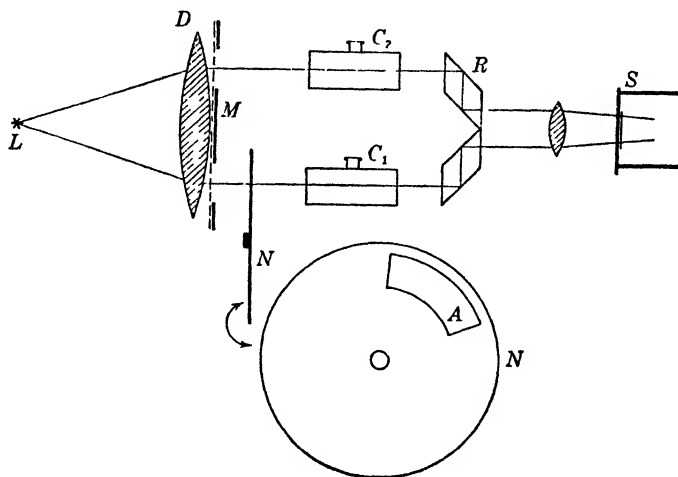

FIG. 65. – The Weigert spectrophotometer (schematic).

L = lamp
D = ground-glass or quartz diffusing screen
N = revolving sector of calibrated variable aperture A
C_1 = cell containing solvent
C_2 = cell containing solution
R = reflecting rhombs
S = slit of spectroscope

of extinction values must be accompanied by information concerning the dispersion of the instrument and the slit width employed. Great care must be taken to ensure cleanliness of the cells, lenses, and prisms, and the liquids used must be clarified by filtration, preferably through a sintered glass membrane.

All visual spectrophotometers suffer from the disadvantage inherent to all visual instruments, *viz.*, the defects of the human eye. As shown in Fig. 69, the eye possesses very low sensitivity at the extreme ends of the spectrum. This fact results in very large percentage errors in matching the intensities of two halves of the field of view. Also, that portion
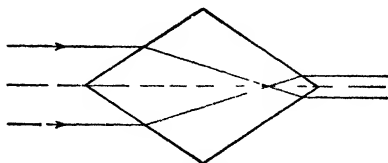
FIG. 66. –The Hufner rhomb, sometimes used instead of the twin rhombs shown in Fig. 65.

of the retina which receives the image of the brighter half of the field tends to become more fatigued than the portion receiving light from the dimmer half, with consequent errors in determination of the match point.   Martin[16] gives an excellent simple discussion of the problem with reference to the original work of Nutting and Koenig (see also McNicholas[74] and Gibson[35]).

PHOTOELECTRIC SPECTROPHOTOMETERS

48. Photoelectric Devices.—The range and precision of the visual spectrophotometer may be increased many times by
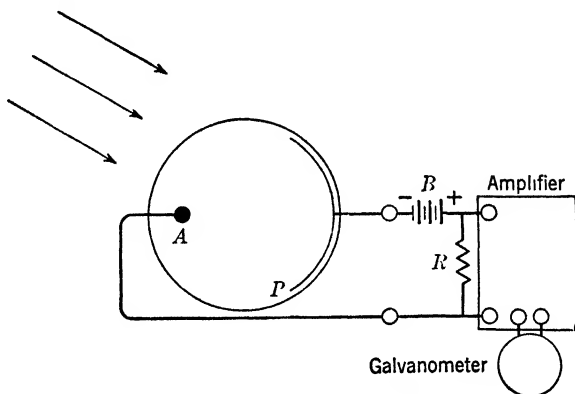
Fig. 67.—The phototube circuit.
A = anode
P = photoemitting cathode
R = high resistance
B = battery

substituting a photoelectric cell, photovoltaic cell, or thermocouple for the fallible human eye (see Gibson[77]).   Before entering into a discussion of the instruments themselves, it may be well to mention the construction and properties of the light-sensitive devices employed.

The phototube or photoelectric cell is, in simplest terms, a vacuum tube containing a plate P coated with a substance like cesium oxide (Fig. 67) which emits electrons when illuminated. The electrons so emitted proceed to an anode mounted in the tube, thereby causing a current to flow through an outside circuit. This current, which may be amplified by electrical means, is taken as a measure of the amount of light striking the photosensitive plate.   Some tubes are sensitive throughout the region

210 to 1,000 mμ, although their response shows maxima and minima over their range (Fig. 69). Further details may be found in texts by Strong,[24] Zworykin and Wilson,[17] Withrow,[18] Müller,[19] Partridge,[20] and Reich.[76]

The photovoltaic, barrier-layer, or photronic cell (Fig. 68) is entirely different in design and principle from the phototube. The photovoltaic cell consists of a metal disk coated on one side with selenium or cuprous oxide whose surface is in turn covered with two transparent layers of metal (Au, Pt, Cu, or Pb), which are protected from the atmosphere by a coat of lacquer. When subjected to illumination, a potential is developed across the boundary between the selenium
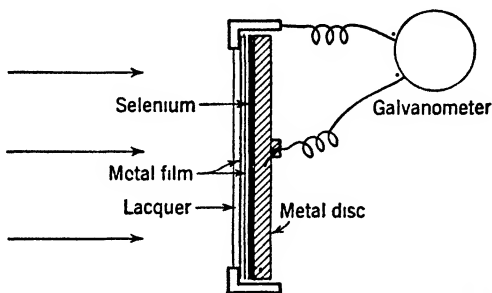
Fig. 68.—The photovoltaic cell (cross section enlarged).

and the conducting film. This potential is of an electronic nature, no chemical transformation being involved, and is of the order of a few tenths of a volt at low intensities. The current generated by the short-circuited cell is proportional to the illumination as well as to the area of the element. This current is about 3 microamp./foot-candle/sq. in. for a typical barrier layer, which is sufficient to permit use of an ordinary galvanometer for measurement of light intensity. No auxiliary equipment is necessary, and indeed, the output of the cell cannot be amplified easily because of the low voltage sensitivity. Whether or not the reproducibility of these cells is sufficient to warrant amplification is questionable.

The output of the selenium barrier-layer cell is said to be somewhat higher than that of the cuprous oxide type,[21] although the principle of operation is similar. The output of a photoemission device such as the cesium oxide phototube is exceedingly small,

but owing to the high internal resistance, the response may be thermionically amplified.

The response of most photoelectric devices is not constant over the entire active area, and it is therefore important that exactly the same region be illuminated every time.   A diffusing screen placed in front of the element will eliminate variations from this source.

The wave-length sensitivity curve of a typical barrier-layer cell shows a maximum in the yellow-green region, but the effective spectral range covers only slightly more than the visible (Fig. 69). For further details see Zworykin,[17] Loewenberg,[22] and Lange.[28]
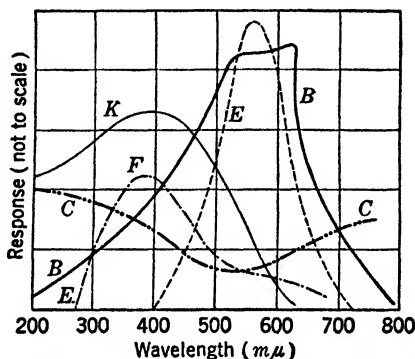
FIG. 69.—Response of photosensitive devices (approximate).

B = photovoltaic cell (electrocell)   K = potassium hydride phototube
C = cesium oxide phototube   E = human eye
                                              F = potassium oxide phototube

Thermocouples are not usually employed for visual or ultra-violet spectrophotometry but are used extensively for the infra-red region.   Data on thermocouples and radiometers is given by Strong.[24]   Brackett and McAlister[25] describe thermopiles that are as sensitive as a typical photovoltaic cell, and whose range extends far out into the infrared.

49. The Cenco Spectrophotometer.—One of the popular instruments for ordinary analytical purposes is the Cenco Spectrophotelometer, shown schematically in Fig. 70.   Because of its simple construction, this instrument is particularly well suited for illustration of certain general principles that will be considered in the following section.   A source L of constant intensity is focused on the entrance slit S_1 of a modified Eagle spectroscope (see Sec. 25).   By turning the crank A, the grating

is simultaneously moved along the axis of the instrument and rotated in such a way that the spectrum is made to move over the exit slit S_2. The latter transmits a narrow band of monochromatic light whose central wave length may be read on the scale W. The cells C_1 and C_2 containing the solvent and solution, respectively, are rigidly mounted on a sliding carriage so that either cell may be placed in the path of the monochromatic
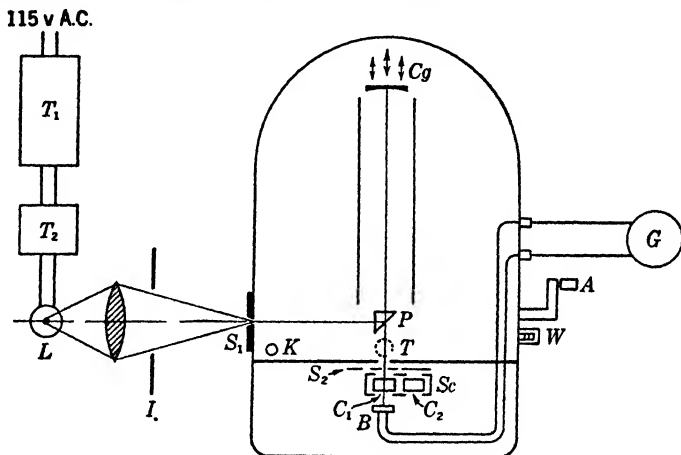

FIG. 70.—The Cenco Spectrophotelometer (schematic).

T_1 = 115/115 volt constant-voltage transformer
T_2 = 115/6 volt transformer
L = 6-volt 108-watt ribbon filament lamp
I = iris diaphragm
S_1 = adjustable entrance slit
K = knob for adjusting width of S_1
P = reflecting prism
C_g = concave reflection grating
T = telescope for viewing spectrum
S_2 = exit slit with three openings for isolation of 20-, 10-, or 5-mμ band
C_1 = cell containing solvent
C_2 = cell containing solution
B = barrier-layer photovoltaic cell
G = galvanometer (1.5×10^{-9} amp./mm.)
W = wave-length scale
A = crank for moving grating

ray. The output of the barrier-layer cell B is measured by the galvanometer G whose reading is proportional to the transmitted intensity. The ratio of successive readings for solution and solvent is equal to the transmission (I/I_o).

50. Experimental Factors Affecting Measurements.—The inherent effects of concentration, temperature, etc., on spectrophotometric observations have been discussed in Sec. 45. In

addition, there are several extrinsic factors that affect the results of observations made with both visual and photoelectric instruments. A few of these extrinsic or experimental factors are listed below.

1. Constancy and reproducibility of the source.
2. Effect of stray light from the grating, etc.
3. Effect of overlapping second-order spectrum (grating instruments only).
4. Purity of monochromatic light produced (slit width).
5. Response of the photosensitive element.
6. Mechanical perfection of the mounting.
7. Reproducibility of the position of the cells.
8. Equivalence and dimensions of the cells, cleanliness, clarity of liquids.

Some of these points are discussed in the following paragraphs.

The first factor cited above concerns the source itself, which in the Cenco instrument is a ribbon-filament bulb powered by a constant-voltage transformer connected to the a.c. mains. Although this arrangement is completely satisfactory in most cases, the fluctuations of the a.c. main may be sufficient in some localities to cause perceptible changes in the light sources. An alternative system is the use of high-capacity storage batteries, which furnish satisfactorily steady voltage but are far less convenient. The incandescent source will show certain irregularities during the first few minutes after it is turned on. These are due to a variety of factors involving expansion and twisting of the filament, heat loss, etc., and it is a good practice to allow at least 5 minutes for the lamp to attain a steady state.

Other sources used in ultraviolet spectrophotometry include the hydrogen discharge tube (Fig. 71), which may be the conventional type shown schematically in the figure or, preferably, the compact all-metal tube described by Allen.[28] The spectrum of the hydrogen discharge tube is nearly continuous from 200 to 350 mμ but is not so constant or so reproducible as the incandescent filament.

A quartz or corex bulb containing a filament run on a 40 or 50 per cent overload will emit sufficient ultraviolet for most work, but the life of such a source is necessarily brief.

Note that null instruments are free from errors due to a fluctuating source.

51. Monochromaticity.—In grating monochromators, there is always danger that some of the light from the entrance slit will reflect from the grating and pass through the exit slit along the monochromatic diffracted ray.   This difficulty is best eliminated by using two diffraction gratings in series as mentioned in the following section, but it may be partly overcome by the use of filters over the entrance slit.   In the Cenco instrument, reflection is at a maximum when the grating is oriented almost normal to the optical axis, in which position blue-violet light is concentrated on the exit slit.   Placing a blue-violet gelatin filter over the entrance slit is found to diminish the amount of stray light to a level comparable with the experimental error of measurement.
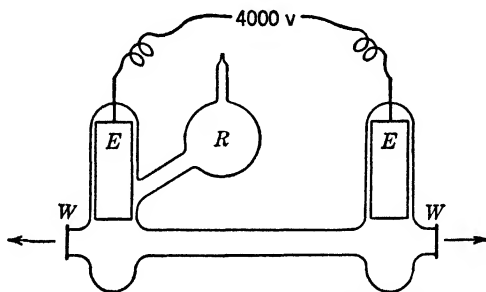
FIG. 71.— The hydrogen discharge tube.
W = quartz window
E = electrode
R = reservoir for hydrogen (3 or 4 mm. pressure)

Stray light is easily detected by employing a mercury-arc source and noting the galvanometer deflection when the wavelength scale is set a few tenths of a millimicron from the wave length of some line in the spectrum.   No deflection should be noted.   The lines of the spectrum also furnish an easy method of checking the wave-length scale.

Preston[29] suggests a very ingenious method of determining the amount of stray light.   The entrance slit is first covered by a horizontal mask which blocks out exactly one-half of the length of the slit.   The intensities I and I_o of solvent and solution are then measured at a given wave length.   A similar mask is then placed over exactly half the exit slit in such a way that all the monochromatic light is cut off.   The only light then reaching the photocell is half the original amount of stray light which can thus be evaluated.   The solvent and solution transmissions

I_{o1} and I_1 are measured for the stray light alone, and the stray light is evaluated by $2 \times I_{o1}$.   The corrected transmission of the sample will be

$$T = \frac{(I - 2I_1)}{(I_o - 2I_{o1})}$$

At the red end of the diffraction spectrum, stray light will be present owing to the overlapping of the ultraviolet portion of the faint second-order spectrum.   Thus when a first-order ray of 760 mμ passes through the exit slit, it will be accompanied by a faint second-order ray of approximately half that wave length, *viz.* 380 mμ.   Although the second-order spectrum is usually much less brilliant than the first order, especially if an echelette grating is employed (see Sec. 23), it is usually necessary to eliminate the ultraviolet and violet of the second order by placing a red filter over the entrance slit.   The magnitude of the second-order error is easily determined by measuring the transmission of two strong dye solutions or filters that are known to absorb completely in the violet or red regions, respectively, and to transmit other wave lengths freely.[72]

A Corning HT yellow filter 2.00 mm. thick transmits only 1.6 per cent at 420 mμ and 1.7 per cent at 405 mμ and may be used to test for stray light in this region.   The Coleman Electric Company[73] recommends a 13-mm. layer of 2.5 per cent aqueous copper chloride to test for the second-order effect, since its transmission is negligible from 720 to 1,000 mμ.   A list of suitable filters is given by Gibson *et al.*[72]

The purity of the monochromatic band that passes through the exit slit depends not only on the absence of stray light but also on the width of the entrance and exit slits.   Thus a very large entrance slit will permit the overlapping of neighboring wave lengths at the exit slit.   The following abbreviated discussion of this problem follows the detailed article of Hogness *et al.*[12]   Hogness first defines slit width in terms of the width in millimicrons which the slit subtends on the spectrum.   Thus the spectral width of the exit slit is simply the wave-length interval it covers.   In the same way, the width of the entrance slit is defined in terms of the width of its image in the projected spectrum.   These effective widths may be calculated from the known optical properties and linear dispersion of
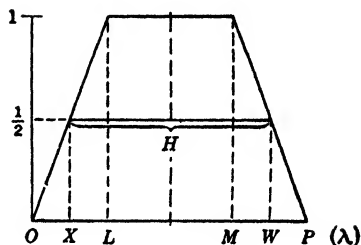
(a)

(b)
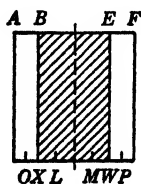
Case 1: $AB = BE = EF = OL = MP$

(a)

(b)
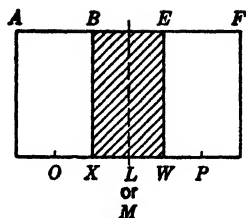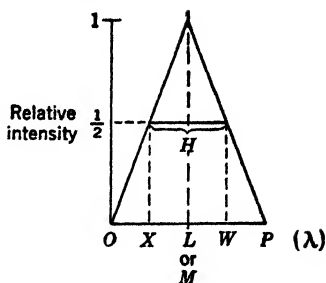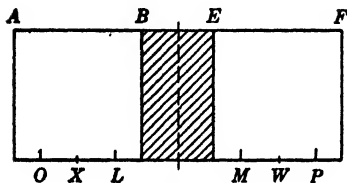
Case 2: $OL = MP = BE$
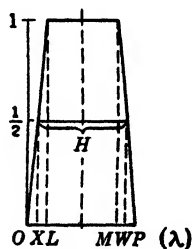$OP = AB + BE$
$LM = AB - BE$
$OP = 2BE + LM$

(a)

(b)

Case 3: $OP = AB + BE$
$LM = BE - AB$
$OP = 2BE - LM$

FIG. 72.—Relation of slit width to monochromaticity.   (*After Hogness.*)
   BE = width of exit slit in terms of λ
AB, EF = width of entrance slit in terms of λ
   OP = width of "monochromatic" band passing through exit slit
   H = width of band whose intensity is more than half the maximum transmitted intensity

the instrument. In Fig. 72, the images AB and EF of the entrance slit are shown projected on the width BE of the exit slit, both widths being expressed in millimicrons. Three cases are illustrated. In the first case, the widths of entrance and exit slits are equal, i.e., $AB = BE = EF$, and if the exit slit is scanned by a hypothetical photometer, the variation of transmitted intensity with wave length for the isolated portion of the spectrum transmitted is found to follow the graph shown in (b). The maximum intensity is found at the center of the exit slit, and the intensity falls off until at wave lengths corresponding to points O and P it becomes zero. If the entrance slit were infinitely narrow, then of course wave lengths would be transmitted only between B and E ("nominal slit width"), but since the entrance slit is large, the spectral images overlap enough to permit wave lengths between O and P to be transmitted.

In cases 2 and 3, the entrance slit is respectively larger and smaller than the exit slit. The intensities of wave lengths passing through the exit slit are plotted in (b). It may be concluded from the three graphs shown that for the general case the wavelength spread OP of the beam passing through the exit slit is given as the sum of the effective slit widths AB and BE. Also,

$$OP = 2(H - LM) + LM$$
$$= 2H - LM$$

where H is the half-intensity width. H itself is often used as a measure of the spectral width.

52. The Effect of Monochromaticity on Transmission Measurement.—The slit width not only governs the monochromaticity of the light from the monochromator, but also has a profound effect on the measurement of the percentage transmission, as shown in Fig. 73. It is for this reason that it is necessary to record dispersion and slit widths whenever reporting transmission or extinction values. In Fig. 73, the actual absorption curve, as determined by another method, is shown as the dot and dash line. With a narrow slit, the spectrophotometer is able to reproduce this curve quite faithfully except where the band is exceedingly sharp (a). With a wide slit, however, the observed curve barely approximates the true curve, and indeed misses one band (c and d) completely. The most significant deduction

that may be made from the three curves is that the percentage transmission measured at a narrow minimum in the curve is governed to a large extent by the width of the slit. In addition, any slight errors in the wave-length setting will cause proportionately greater errors in the observed transmission when the curve slopes sharply. The necessary width of the exit slit depends largely upon the fineness of the band structure of the absorption spectrum that is to be studied. Physical researches may require a monochromatic beam whose spectral width is of the order of a millimicron or less, but special equipment is required for illuminating such a narrow aperture. Ordinary colorimetric and analytical procedures, however, seldom necessitate an effective
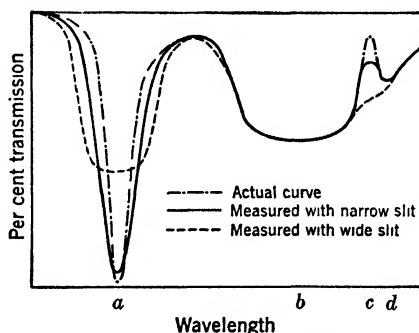
FIG. 73.—Effect of slit width on transmission curve.

slit width of less than about 5 mμ. (The spectrophotometric determination of certain of the rare earths is an exception, owing to the exceedingly narrow absorption bands.)

The converse of the preceding deductions may be expressed in the following way: the percentage transmission or extinction is most reproducible when measured at a low point in the transmission curve where the slope is not changing rapidly with wave length, *i.e.*, point *b* in Fig. 73.

Pineo[30] discusses errors of this general type in a discussion of Hardy's instrument.

53. Other Factors Affecting Transmission Measurement.— Cleanliness of the cells is very important, and it is recommended that cells be cleaned in concentrated nitric acid or aqua regia. Dichromate solutions should not be used, owing to their tendency to be adsorbed by glass. A cotton swab may be used to remove large particles, and the cells should be rinsed several times before
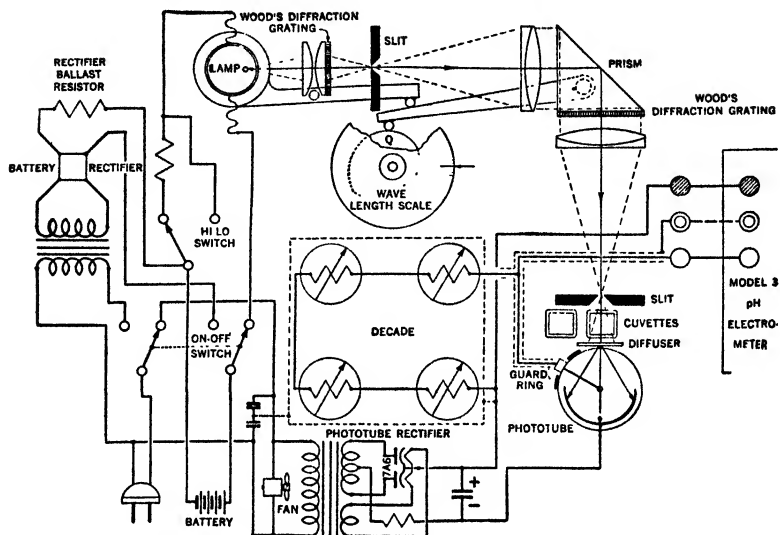
FIG. 74a.--The Coleman Model 10 double-monochromator spectrophotometer.
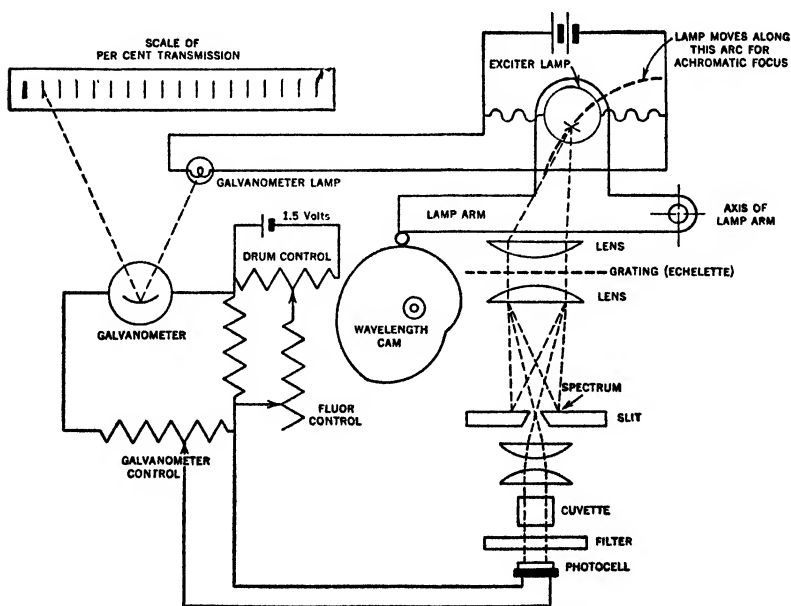

FIG. 74b.--The Coleman Model 11 spectrophotometer.   This is an instrument especially designed for analytical use where a narrow monochromatic band is not essential.

drying. The sensitivity of many colored materials to minute traces of acid makes this latter precaution especially important. Solutions and solvent must be completely free from suspended matter which is easily removed in most cases by filtration through sintered glass or by centrifugation. The filled cells are carefully wiped clean with lintless cloth or bibulous paper. Fingerprints or bits of lint on the cell windows may cause unexpectedly large errors. The liquids themselves should not be too volatile and should not contain dissolved gases which may tend to form bubbles.

The precision with which the cells are constructed by optical manufacturers in this country leaves little to be desired. It is advisable, however, to check the equivalence of two cells by measuring the transmission of identical samples. One cell is usually reserved for the sample exclusively, and the other is always used for the solvent.

The transmission of most transparent materials is influenced by temperature, although the effect of ordinary variations in room temperature is seldom serious enough to require correction except in work of the highest accuracy. The photo element, however, is more sensitive, and in some cases it may be necessary to keep the entire instrument in a constant-temperature room.

54. Other Photoelectric Spectrophotometers.—The Cenco instrument mentioned previously is well suited for use in approximate analytical work, but its spectral range is somewhat limited. With a special illumination system, however, it is possible to measure transmissions as low as 328 mμ, which is the wave length of the vitamin A absorption band. A minimum slit width of about 3 mμ is possible. The double-monochromator spectrophotometer designed by R. W. Wood and manufactured by the Coleman Electric Company is a very compact instrument with a range from 350 to 1,000 mμ (Fig. 74*a*). The monochromator is especially ingenious in that it practically eliminates stray light and greatly reduces the second-order effect. A cesium oxide phototube and a thermionic amplifier are used in conjunction with a potentiometer that gives null readings. A storage battery supplies current to the small bulb used as a source.

The Beckman instrument (Fig. 75) is said to have a range of 200 to 2,000 mμ, which indicates a greater versatility than either of the above-mentioned instruments. An automatic

slit mechanism eliminates the principal objection to a prism monochromator, which is the variation of dispersion with wave length. The half-intensity width of the monochromator band is said to be 5 mμ in the ultraviolet, 2.5 mμ in the visible region, and 5 to 10 mμ in the infrared region.
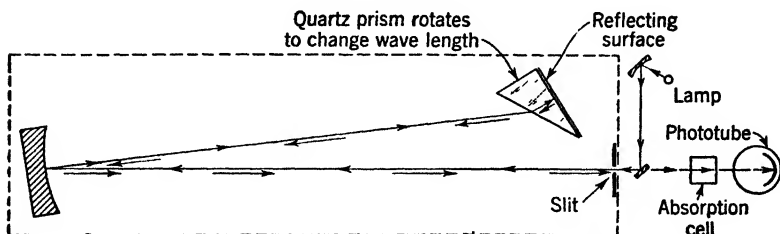

FIG. 75.—The Beckmann spectrophotometer—range 200 to 2,000 mμ. (This range is achieved in steps. Several accessory systems are used.)
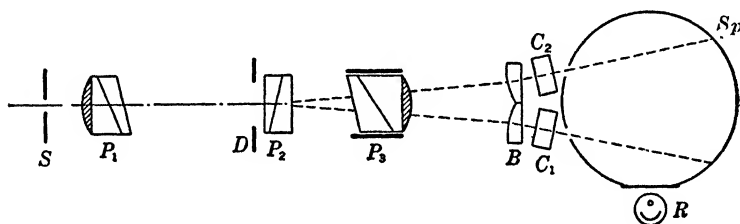

FIG. 76.—The Hardy color analyzer (simplified).

S = exit slit of van Cittert monochromator
P_1 = photometer prism in rotating mount, whose position is controlled by a cam
D = diaphragm
P_2 = Wollaston prism
P_3 = flicker prism in rotating mount attached to synchronous motor
B = split lens
C_1 and C_2 = cells for solvent and solute
Sp = integrating sphere
R = phototube

When the intensities of the two rays entering the integrating sphere are not equal because of absorption by the solution in C_1, the phototube current shows pulsations due to the revolving flicker prism P_3. This pulsating current is amplified and made to rotate the photometer prism P_1 until the intensities of the two rays are equal when the pulsations cease. The tangent of the angle through which prism P_1 is turned is a measure of the absorption occurring in C_1. A plot of transmission vs. wave length is made by an ingenious automatic mechanism.

An elaborate automatically recording null spectrophotometer (Fig. 76) designed by Hardy[31] is manufactured by the General Electric Company. It is more accurate and versatile than either of the small instruments mentioned above and is capable of tracing the most complicated absorption curve in a few min-

utes or so. The Hardy instrument is useful only in the visual
range, however. A. Hilger manufactures a compact but elabo-
rate instrument whose sensitivity is claimed to be ten times
that of the best visual or photographic method.[11] Many excel-
lent instruments have been built by various research workers and
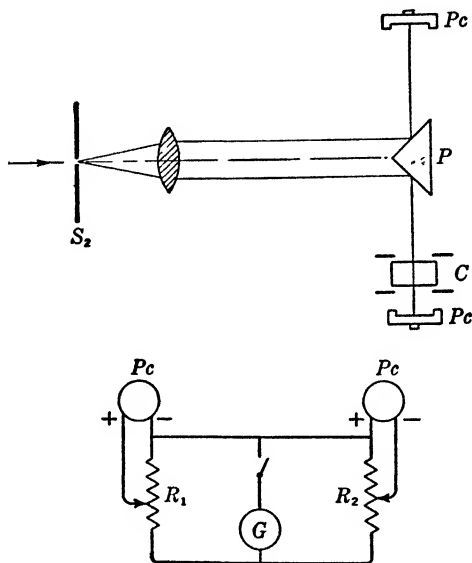reported in the literature. The most notable contribution is

FIG. 77.—Spectrophotometer.   (*After Yoe.*)

S_2 = exit slit of monochromator
P = dividing prism
P_c = barrier-layer cell
C = cell containing sample
R_1 = 2,000-ohm calibrated slide-wire
R_2 = 6,000-ohm compensating variable resistor
G = 5×10^{-10} amp./mm./M galvanometer (r = 1,417 ohms)

that of Harrison,[32] who devised a recording spectrophotometer
for rapid measurements over the range 200 to 1,000 mμ.

Among the nonrecording spectrophotometers reported in the
literature is the high-precision instrument used by Hogness.[12]
The instrument covers the range 220 to 780 mμ with an effective
slit width of the order of 1 mμ. In the article cited above,
Hogness gives a good account of some of the problems of spectro-
photometry. Deck[33] describes a somewhat similar instrument
which is claimed to measure extinction coefficients to 0.1 per cent,
and Jacobson *et al.*[34] offer still another modification. A very

comprehensive and critical account of the theory, design and operation of various types of commercially available photoelectric spectrophotometers is given by Gibson.[77]

Several designs for "null" instruments are found in the literature.   These generally consist of two photocells or barrier-layer cells, one of which receives light that has passed through the solvent whereas the other receives light transmitted through the colored solution.   The ray that has passed through the solvent is reduced in intensity by means of a rotating sector, neutral wedge, or other device until the output of the two photocells is balanced.   Intensities are determined from the setting of the wedge or sector.   The well-known Von Halban instrument operates on this principle.[36] [37]

One of the simpler null instruments is that of Barton and Yoe,[21] who employ an electrical method of balancing the output of the two barrier-layer cells (Fig. 77).   Although this method is simple, it is open to the objection that the two photosensitive elements may not respond to illumination in exactly the same way.

Designs for two photoelectric instruments employing neutral wedges are given by Miller[39] and Drabkin.[40]   General reviews of apparatus and methods are given by the Optical Society of America Progress Committee,[41] by Partridge[20] and Gibson.[77]

SPECTROGRAPHIC METHODS

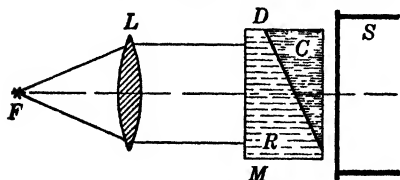**55. The Wedge Spectroscope.**—The simplest and at the same time the least accurate type of visual instrument is the wedge spectroscope shown in Figs. 78 and 79.   The colored solution is placed in part C of a glass container divided into two wedge-shaped halves by a cemented diagonal piece D. The other wedge-shaped section is filled with solvent R, whose function in this case is to prevent the dispersion that would occur in a prism-shaped cell.   The cell is placed immediately in front of a spectroscope slit and illuminated by parallel rays

Fig. 78.—The wedge spectroscope.
F = filament of projection bulb
L = condenser
M = wedge cell
D = glass diagonal wall
C = portion containing solution
R = portion containing solvent
S = spectroscope

from a concentrated filament bulb or other source F.   The resulting spectrum viewed through the spectroscope will have an appearance similar to that shown in Fig. 80.   In the spectral range where the dye is quite transparent, as in the red region for the case illustrated, even the large thickness of solution in the upper part of the cell will transmit sufficient light to be visible in the spectrum.   In the spectral region where the solution absorbs strongly, however, even the thin layer at the bottom of the cell
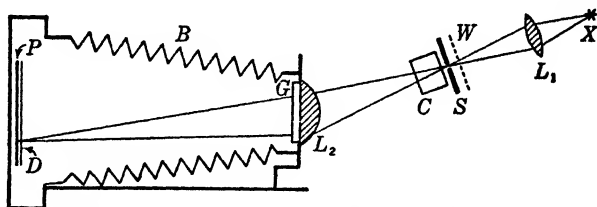
FIG. 79   The simple wedge spectrograph.

X = ribbon filament lamp
L_1 = condenser
W = neutral wedge (if used)
S = slit
C = cell (plain, wedge, or step type)
L_2 = camera lens
G = plane transmission grating
B = camera
P = plate or film
D = transparent coordinate net marked in wave-length units
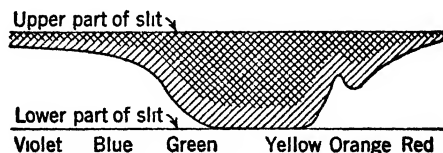
FIG. 80.—The wedge spectrum.

will not transmit enough light to register in the spectrum, as in the green region shown in the figure.   The diffuse dividing line between the dark and light portions of the spectrum furnishes an approximation to the shape of the transmission curve but is modified by the varying spectral sensitivity of the eye or photographic plate.   The actual transmission values themselves are not measurable by this method.

An alternative variation of the wedge principle is to place a neutral wedge of dark glass, gelatin, or photographic emulsion over the slit and use a parallel-walled absorption cell.   This method is used not only for qualitative study of absorption

spectra but also in measuring the spectral response of photographic films.[42][43]

Miller[39] describes a very ingenious optical system that accomplishes the purpose of the wedge, but whose working principle is a step diaphragm. Absolute neutrality throughout the spectrum is thus attained, and very accurate adjustment of the wedge gradation is possible. These factors are very difficult to control in the construction of dark-glass, lampblack plus gelatin,[44] or sputtered metal wedges.[15][16]

O'Brien's method[47] of contrast printing may be employed to increase the sharpness of the diffuse edges of the photographed wedge spectrum. A related procedure that is different in method is described by Holiday.[48] A spectrograph is employed, and a cell containing the sample is placed over the slit. Exposures are made, using a continuous source, while the plateholder is moved upward at a steadily increasing rate by revolving a spiral cam. The resulting spectrogram will resemble that obtained by the use of a neutral wedge and is particularly useful for revealing narrow bands and detailed structure.

	Width (mm)	Relative Transmission
g	$\frac{1}{2}$	100
f	$\frac{1}{4}$	50
e	$\frac{1}{8}$	25
d	$\frac{1}{16}$	12.5
c	$\frac{1}{32}$	6.25
b	$\frac{1}{64}$	3.12
a	$\frac{1}{2}$	100 (For solution)

FIG. 81.—The multiple slit.

56. The multiple-slit spectrophotometer manufactured by Kipp and Zonen embodies a novel principle analogous to that of the neutral-wedge instrument. Light from a continuous but necessarily constant source, such as a hydrogen discharge tube, is gathered by a double-rhomb system and passed through two identical cells containing solvent and solution. Light that has passed through the solution enters slit a of the multiple slit shown in Fig. 81, which replaces the usual slit of the spectro-

graph.   Light that has passed through the solvent enters slits
b, c, d, e, f, and g, which have the approximate widths shown
in the figure.   The resulting spectrogram consists of a series of
spectra corresponding to the seven slits (Fig. 82).   The top
spectrum will be the absorption spectrum of the solution, and
slits b, c, d, e, f, and g form six reference spectra corresponding
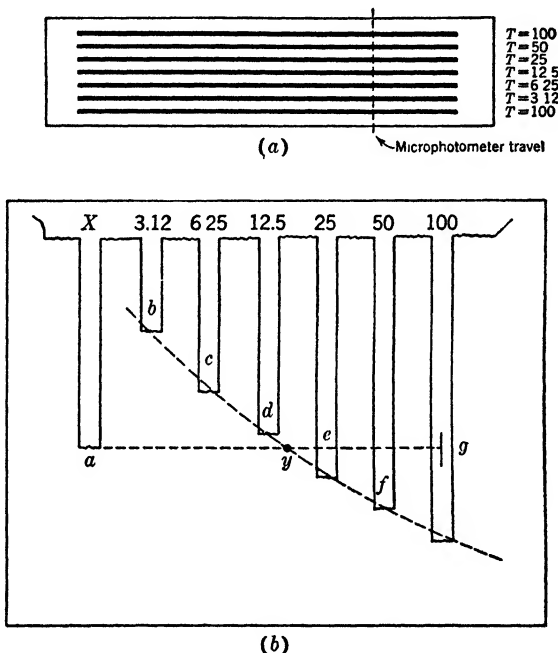to percentage transmissions of 3.12, 6.25, 12.5, 25, 50, and 100,
respectively.

FIG. 82.—The use of the multiple slit: (a) spectrogram showing travel of micro-
photometer; (b) microphotometer tracing (schematic).

To find the percentage transmission of the solution at any
wave length, it is necessary to run a recording microphotometer
across the seven spectra at that wave length.   The photometer
record will resemble that shown in Fig. 82b.   A curve is drawn,
as shown, through the deflections corresponding to the six solvent
slits, and the transmission of the solution may be obtained by
drawing a line ag as shown.   Since y falls between spectra d
and e, the transmission must be between 12.5 and 25.   It may
be measured more exactly by graphical interpolation.   Consid-

eration of the relations involved shows that yg is proportional to $\log (I_o/I)$, the proportionality factor being found by the following procedure: when $yg = fg$, then $I = 0.5$ and $\log \dfrac{I_o}{I} = 0.69$. Thus

$$\log \left(\frac{I_o}{I}\right) = 0.69 \left(\frac{yg}{fg}\right)$$

or, using the Beer-Lambert expression,

$$k = \frac{0.69}{cl} \left(\frac{yg}{fg}\right)$$

It is thus possible to measure k, $E_{1\,cm}^{1\%}$, or ϵ by simple linear measurement on a photometer record.

The disadvantages of the method are obviously the large slit width, with consequent loss of resolution, and the fact that a complete absorption curve cannot be constructed without a great deal of troublesome work with a photometer. The principal advantages are the compactness and availability of the equipment and the ease with which a single quantitative determination may be made at any one wave length.

57. Other Simple Photographic Methods.—If a cell containing a colored solution is placed in front of the slit of a spectrograph, the spectrum of a continuous source will show dark areas or bands corresponding to the spectral regions where absorption is strongest. These bands will not in general show sharply defined boundaries. The width of a given band will tend to vary with

1. The concentration of the absorbing material.
2. The length of the cell containing it.
3. The exposure time.
4. The brightness of the source.
5. The characteristics of the photographic emulsion.
6. The photographic processing.

Given a solution of known concentration, the effect of decreasing the thickness of the column of absorbing liquid is shown in Fig. 83. Note that the effect is similar to that produced by a wedge and that the results will be purely qualitative. Alteration of the length of the cell is best accomplished by the Baly tube shown in Fig. 84, which is graduated in terms of l or $\log l$. The Baly tube may be used for rough quantitative determinations

according to the historical method of Hartley. The wave lengths of the edges of absorption bands are plotted on a wavelength scale vs. the length of the cell or logarithm of this length (see Baly[50]).

Owens[51] has recently introduced a modification of Victor Henri's method (1919) of measuring extinction. The equipment
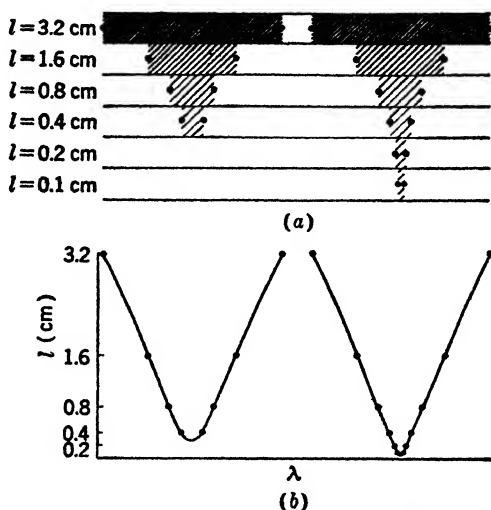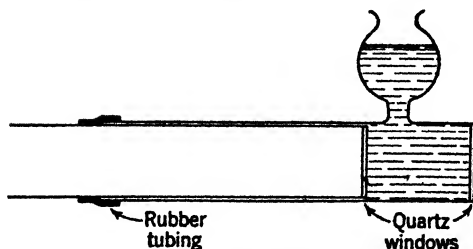

FIG. 83.—The use of the Baly tube.

FIG. 84.—The Baly tube.

required is available in any laboratory equipped for quantitative emission spectroscopy, *viz.*, with a spectrograph and a densitometer. The only special apparatus needed is a small quartz cell for holding the sample. The first step in the analysis is to determine the characteristic curve of the emulsion by methods already referred to in Sec. 35. The spectrum of a steady source is photographed, with the filled cell placed in front of the slit

of the spectrograph. A second exposure is made when the cell contains only the solvent. The blackening of the developed plate is then measured by means of a densitometer, and the intensity values are calculated graphically from the characteristic curve. If I_o and I represent the intensity transmitted by the solvent and the solution, respectively, at some wave length of minimum transmission and I_2 represents the maximum intensity transmitted by the solution at any wave length, then

$$\log_{10} \frac{I_2}{I} - \log_{10} \frac{I}{I_o} = kcl$$

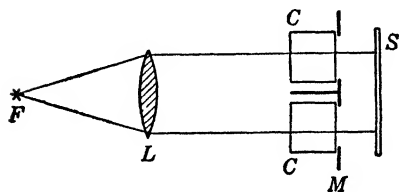The value I_2, measured at the wave length where the sample transmits nearly all incident light, corresponds to the internal standard used in quantitative emission spectroscopy. Its purpose is to permit correction for any small differences in exposure time. Owens claims that k may be measured to 0.006 for values between 0.08 and 0.12. The extinction coefficient may, of course, be measured for every wave length, and a curve may be plotted vs. wave length, but for quantitative work it is only necessary to make measurements at one wave length, usually that of maximum absorption.

Fig. 85.
F = source
L = condenser
C = cell
S = slit of spectrograph

Ruehle and Jaycox[52] propose a similar method employing a binary slit and two identical cells as shown in Fig. 85. The transmitted intensities at any wave length may be measured and calculated as above.

58. The Spekker ultraviolet photometer is illustrated schematically in Fig. 86. Light from source X, which may be a hydrogen discharge tube or a spark between tungsten-steel or uranium rods, is split into two beams by the quartz-rhomb system R_1. The beams are made parallel by lenses L_1 and L_1 and pass through the apertures D_1 and D_2 into cells C_1 and C_2. The rhomb system R_2 causes the two rays to pass through slit S of a spectrograph and to be focused one above the other in the plane of the spectrum. Cell C_2 contains the absorbing solution

and cell C_1 the solvent   The amount of light passing through cell C_1 may be varied by means of the variable rectangular aperture D_1 which is opened or closed by moving the drum M, graduated in extinction units
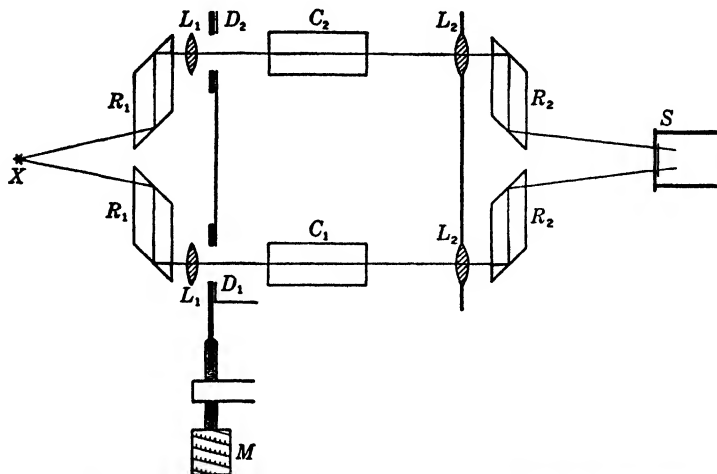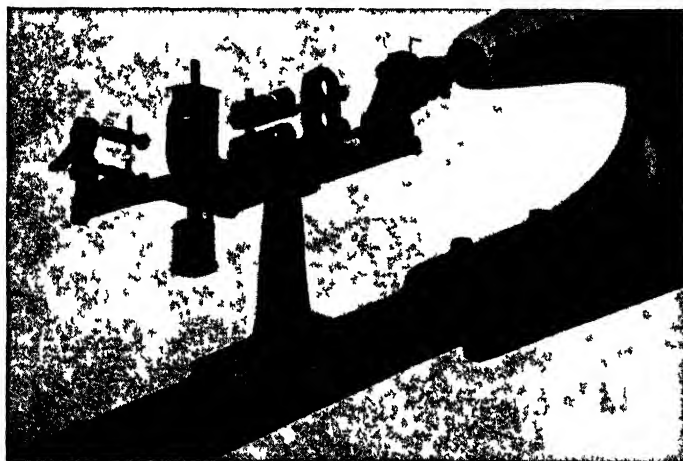

Fig 86 —The Hilger Spekker photometer (schematic)

Fig. 87 —The Hilger Spekker ultraviolet photometer

If cell C_2 contains a solution that absorbs light only in the region 240 to 265 mμ, then the darkening of the photographed plate will be the same for the adjoining solvent and solution spectra at all wave lengths except in the region 240 to 265 mμ.
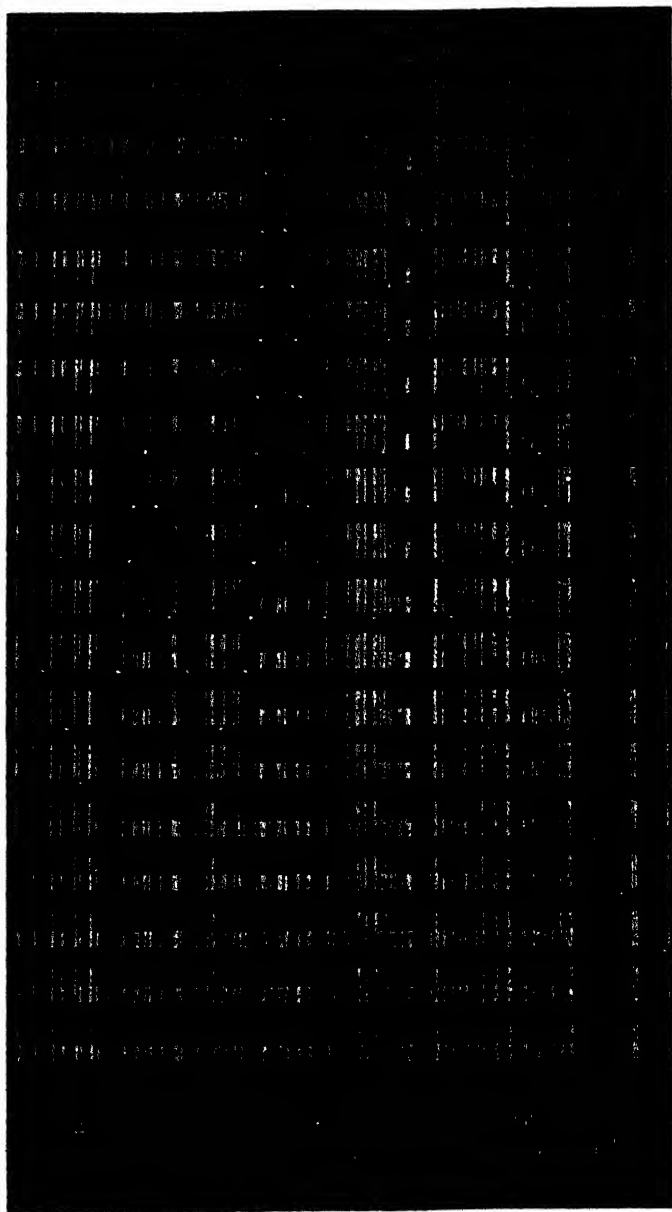
Fig. 88.—Absorption photograph of benzene (in hexane) taken with the Spekker ultraviolet photometer and medium quartz spectrograph. (*Courtesy of Jarrell-Ash Company and Adam Hilger, Ltd.*)

In this region, more light comes through the solvent than through the solution, with the result that the solvent spectrum will be blacker.   The two spectra may be made to match, however, by closing the diaphragm D_1.   After calibration, the scale of drum M may be made to read log (I_o/I) directly.

In practice, a series of 16 or more pairs of spectra are photographed successively on a single plate as the setting of drum M is changed in recorded steps.   The plate is then developed and "spotted."   The latter process consists of marking the points where the blackness of adjoining solvent and solution spectra is equal.   These marks give the form of the absorption curve, and
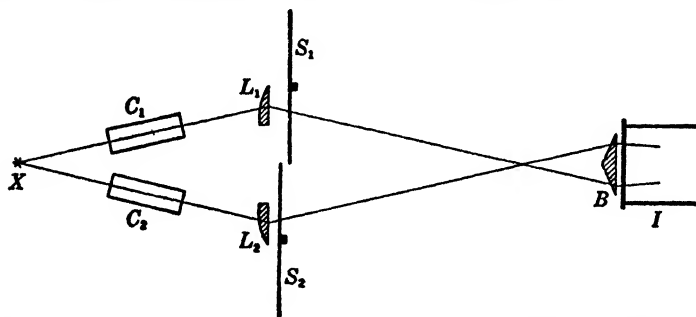

Fig. 89.—The sector photometer Schematic   (*After Hilger instrument*)

$$X = \text{source}$$
$$C_1 \text{ and } C_2 = \text{cells for solvent and solution}$$
$$L_1 = \text{prismatic lens}$$
$$S_1 \text{ and } S_2 = \text{revolving sectors}$$
$$B = \text{biprism}$$
$$I = \text{spectrograph}$$

the extinction value for any point will be given by the recorded reading of the drum M for that particular spectrum.   The appearance of the typical spotted plate is shown in Fig. 88.   Note the photographically superposed wave-length scale which is printed on the film automatically.

Even when the spotting process is accomplished with the help of a densitometer, the accuracy of the method is not so great as that of a good photoelectric spectrophotometer.   Twyman and Alsopp[11] give an account of the instrument, which is used a great deal in chemical research.   Spectra covering a wide density range may be made in about 15 minutes.   Cells from 1 to 100 mm. are accommodated.

59. Sector photometers are historically (1910) forerunners of the above-mentioned Spekker instrument.   They are optically

somewhat similar but differ in that the diaphragms D_1 and D_2 are replaced by revolving adjustable sector disks (see Fig 89).
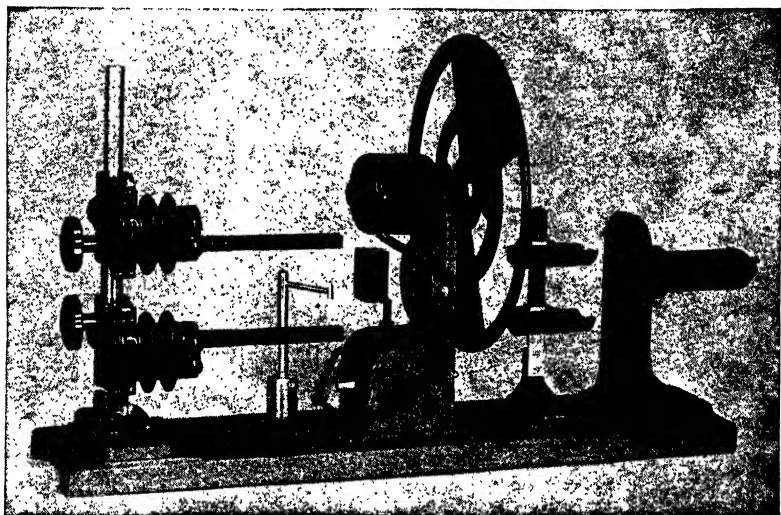

Fig. 90.—Ultraviolet sector photometer, arranged for arc illumination. (*Courtesy of Bausch and Lomb Optical Company.*)
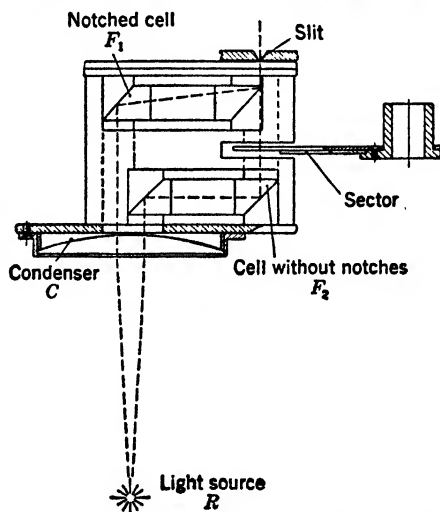

Fig. 91.—The echelon cell. (*Courtesy of Adam Hilger, Ltd., and Jarrell-Ash Company.*)

The Bausch and Lomb sector disk is shown in Fig. 90. The sector openings are adjustable, and the attached scale reads in

density units.   All sector instruments possess the disadvantage of mechanical moving parts.

60. The Hilger Echelon Cell.—This instrument is designed to permit more rapid spectrophotometric analysis by the foregoing procedure by reducing the number of necessary exposures.   In effect, it is a cell composed of 10 small cells whose length varies in steps of constant ratio (Fig. 91).   The solution is placed in a notched cell (Fig. 92) and the solvent in an identical cell without notches.   Light from the source traverses both cells and is passed into the slit of a spectrograph.   Light that has passed through the solution cell strikes the slit in alternate rays whose spacing corresponds to the protruding "teeth" in the side of the cell.   The rays that have traversed the solvent cell pass between the teeth of the notched solution cell in such a way that the slit is illuminated by pairs of adjacent rays from the two cells.
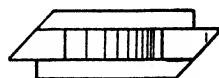
PLAN
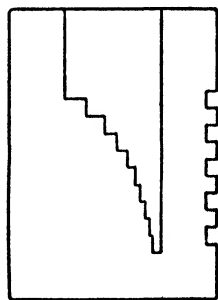
Since the length of solution traversed varies along the height of the cell, one setting of the sector aperture gives 10 pairs of spectra of varying intensity.   This results in a considerable saving of time and reduces the possibility of photochemical effects.   The accuracy is somewhat less than that of the simple Spekker or sector method, however, and solutions of

ELEVATION
Fig. 92.

fairly high absorbing power must be used because the maximum cell thickness is only 1 cm.   For details, see Twyman and Allsop,[11] Twyman, Spencer, and Harvey,[53] and Twyman.[54]

61. Light Sources for Ultraviolet Photographic Photometry.— The two requirements of continuity and absolute constancy that are demanded by direct photoelectric methods are not so essential in photographic spectrophotometry.   The most frequently employed source is a high-tension condensed spark between tungsten-steel rods or between rods of uranium.   The spark spectrum of either of these two sources appears almost continuous because of the number of lines.   The tips of the electrodes are ground to sharp wedge-shaped points, which are made collinear with the optical axis of the instrument.   This reduces the effect of "wandering."   An arc between tungsten-steel rods or between

carbon rods treated with uranium nitrate and ammonium molybdate may also be used, but it is less desirable, not only because of the tendency to wander but also because the rapid consumption of the electrode necessitates frequent adjustment of the gap.

A hydrogen discharge tube may be used as a source for the Spekker photometer, but, owing to the stroboscopic effect, it is not usually used with any of the rotating sector instruments. The continuous spectrum of hydrogen makes the fine structure of a complex absorption spectrum much easier to "spot," but the discharge tube demands considerable extra equipment and is short-lived.[55,56] These same disadvantages hold true for the underwater spark described by McNicholas,[57] which consists of a high-frequency spark gap in a specially constructed chamber through which a continuous flow of distilled water is maintained. The underwater spark gives an intense continuous spectrum that covers the entire transmission range of quartz.

APPLICATIONS OF SPECTROPHOTOMETRY

62. The spectrophotometric curve may or may not identify an absorbing substance, for it is conceivable that two entirely unrelated materials might exhibit the same type of absorption. The shape of a complex curve is nevertheless a good criterion of identity and is much used in the analysis of complex compounds such as vitamins and biological materials in general. The absorption spectrum frequently reveals the presence of chemically similar impurities in a sample of supposed purity.

Holmes and Scanlan[58] give a detailed account of the visual spectrophotometric identification of dyes and mention a criterion of identity that appears to be more dependable than the wave length of the absorption maximum. This is the absorption ratio, defined as $E_{\lambda 1}/E_{\lambda 2}$ where λ_1 and λ_2 refer to arbitrarily selected wave lengths on either side of the absorption maximum. This absorption ratio may also be used for identifying other materials.

The Beer-Lambert law enables accurate quantitative determinations to be made on small samples of liquids or dissolved solids, the sensitivity depending largely on the absorbing power. It is customary to determine extinction coefficients at a wave length where the absorption is strongest, provided that the absorption curve is sufficiently wide at that point (see Sec. 52).

It is obvious that absorption may be increased by increasing the length of the cell employed, but this procedure also tends to increase errors due to stray light.

The typical quantitative procedure involves the following steps: preparing of spectrophotometric curves at three widely different concentrations, calculating specific or molecular extinction values at the chosen wave length, and then noting whether or not they are equal. If the preceding values are not equal, Beer's law does not hold, and it is necessary to plot a curve of K or E vs. concentration. The quantitative determination is made by applying the observed value of (I_o/I) of the unknown
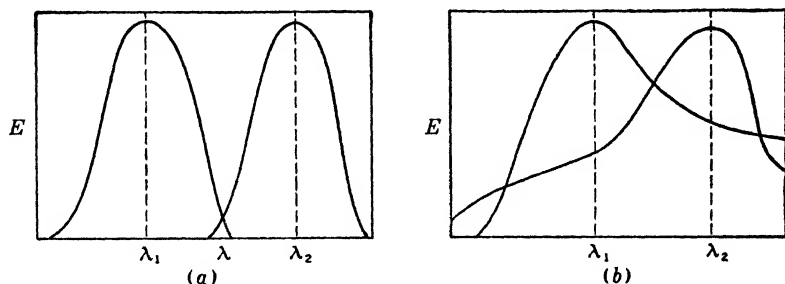

Fig. 93.

solution to the curve or by calculating concentration from the Beer-Lambert equation. The optimum range of concentrations over which the method is applicable obviously varies with the substance to be determined, but most of the published work lies within the range of 0.00001 to 2.00 per cent, although some workers have determined much larger concentrations.[59]

The spectrophotometric method has two advantages over the colorimetric methods discussed in Chap. III. It permits selection of the proper wave length for comparison, and it is applicable to the simultaneous determination of more than one component. Details of the theory and practice of such multiple analyses are given by Weigert[60] and others.[61][62,63] There is obviously no difficulty in determining two components when their absorption spectra do not overlap (Fig. 93a). It is necessary in most cases, however, to allow for overlapping of the type shown in Fig. 93b. According to the Beer-Lambert law, at wave length λ_1 or λ_2

$$\text{(I)} \qquad E_\lambda{}^A = K_\lambda{}^A C^A \qquad \text{and} \qquad E_\lambda{}^B = K_\lambda{}^B C^B$$

where the superscripts indicate the two components. The measured value of E at wave length λ_1 will be

(II) $\qquad E_{\lambda_1}{}^{tot} = E_{\lambda_1}{}^A + E_{\lambda_1}{}^B = K_{\lambda_1}{}^A C^A + K_{\lambda_1}{}^B C^B$

Similarly, at wave length λ_2

(III) $\qquad E_{\lambda_2}{}^{tot} = E_{\lambda_2}{}^A + E_{\lambda_2}{}^B = K_{\lambda_2}{}^A C^4 + K_{\lambda_2}{}^B C^B$

From Eq. (II),

(IV) $$C^B = \frac{E_{\lambda_1}{}^{tot} - K_{\lambda_1}{}^A C^A}{K_{\lambda_1}{}^B}$$

Substituting Eq. (IV) in Eq. (III),

$$C^A = \frac{K_\lambda{}^A E_{\lambda_2}{}^{tot} - K_\lambda{}^B E_{\lambda_1}{}^{tot}}{K_{\lambda_1}{}^B K_{\lambda_2}{}^4 - K_\lambda{}^B K_{\lambda_1}{}^4}$$

Thus by measuring the true values of K with pure compounds and by observing the extinction of the mixed sample at two wave lengths, it is possible to calculate the concentration of either component.

INFRARED AND RAMAN SPECTRA

63. Near-infrared spectrophotometry has long been used as a method of determining the structure of organic molecules but has only recently come into prominence as an analytical tool. The utility of infrared spectroscopy lies in the fact that the wave lengths of infrared absorption bands are characteristic of the absorbing *molecule* and of the various *groups* in the molecule. Thus if an organic compound shows an absorption band in the vicinity of 2,750 mμ, it probably contains a hydroxyl group, whereas a band at 4,450 mμ similarly indicates a nitrite group. With the help of a little chemical evidence, it is thus possible to effect a qualitative analysis of complicated organic substances. It is also possible to perform quantitative analyses by measuring extinction values in the same way as in visual or ultraviolet spectrophotometry. Traces of water may be determined in organic solvents. Isomers and tautomeric species may be distinguished and quantitatively determined. For instance, as little as 0.3 per cent 1,2-dibromopropane may be detected and quantitatively determined in 0.1 cc. 1,3-dibromopropane.[38] Because of the fact that the absorption bands are due to mole-

cules and groups of atoms within the molecule, the method is particularly useful in the study of polymerization and resins. The appearance or disappearance of various linkages may be followed closely during polymerization, a feat impossible by strictly chemical means.

64. Instruments for Infrared Spectrophotometry.—A grating spectrograph and specially sensitized photographic plates will permit photographing the spectrum as far as 1,300 mμ (1.3 μ). Beyond this wave length, it is necessary to use an infrared spectrophotometer employing either a rock-salt or fluorite prism, or, better, a specially designed echelette grating ruled on polished copper. The source commonly employed is a Globar which is simply a water-jacketed incandescent lamp whose filament is either a platinum ribbon or a rod of carborundum. A thermocouple, thermopile, or radiometer is used as the photosensitive element, and the entire assembly resembles, in principle at least, a typical photoelectric spectrophotometer (Fig. 94).

There are several problems inherent to infrared spectroscopy that have long proved barriers to more widespread use of this highly desirable analytical method. (1) The exceedingly low energy of the infrared necessitates the use of photosensitive devices of great sensitivity. Only in recent years have sufficiently sensitive means been found for detecting and measuring infrared radiation. (2) The next major difficulty is the lack of dispersion of prism instruments. An echelette or wire grating gives much higher dispersion, but the various orders of spectra produced may interfere in the desired spectral regions. (3) The infrared absorption of water and water vapor necessitates use of nonaqueous media entirely and elimination of water vapor (and carbon dioxide) from the optical path.

Space does not permit a description of the various types of infrared spectrophotometers and their manipulation, but the design by Wright[3] deserves mention inasmuch as it is one of the very few instruments suitable for routine analytical work. The working principle of the Wright infrared spectrophotometer is shown schematically in Fig. 94. Infrared rays from the Globar *A* are reflected by the concave mirror *B* and pass to the entrance slit *D*. *C* is an absorption cell with rock-salt windows. The rays are then reflected by the plane aluminized mirror *E*, collimated by the concave mirror *F*, and passed through the rock-salt

prism G. The plane mirror H is mounted on a movable platform I which is slowly rotated by a motor and gear train. The infra-red spectrum produced by this modified Littrow system is slowly moved across the exit slit J, and the selected monochromatic band is focused by the elliptical mirror K on a thermopile L. The output of this thermopile is recorded by an amplifying and recording galvanometer[61] synchronized with the revolving turn-table I. The entire instrument is protected by an airtight sheet-metal box containing a drying agent to remove water vapor.
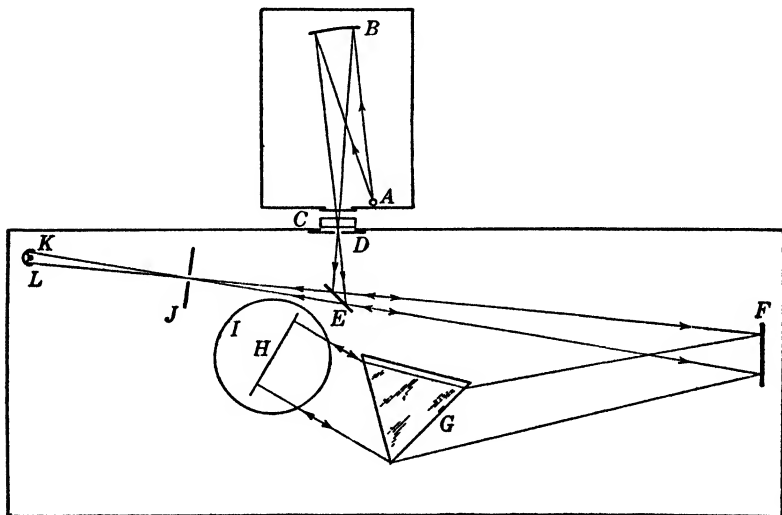
FIG. 94.—Infrared spectrophotometer.   (*After Wright.*[38])

Absorption curves from 2 to 14 μ are recorded automatically in 25 minutes, the recording starting at the longer wave-length end.

Cells of polished rock salt are constructed according to the design of Gildart and Wright,[65] with thicknesses of 1, 0.1, and 0.01 mm. Pure liquids or solutions in carbon disulfide or carbon tetrachloride are generally used. The latter solvents are unusually transparent in the infrared region.

In lieu of further discussion of this promising new analytical tool, the following references are recommended for study:

1. N. WRIGHT, "Applications of Infra-red Spectroscopy to Industrial Research," *Ind. Eng. Chem. Anal. Ed.*, **13**, 1 (1941).

2. R. B. BARNES and L. G. BONNER, "A Survey of Infra-red Spectroscopy," *J. Chem. Ed.*, **14**, 564 (1937).

3. G. P. M. SUTHERLAND, "Infra-red and Raman Spectra," Methuen & Co., Ltd., London, 1935.

4. R. B. BARNES, L. G. BONNER, and E. U. CONDON, "Identification of Bands and Groups," *J. Chem. Phys.*, **4**, 772 (1936).

5. P. LAMBERT and J. LECOMPTE, *Ann. phys.*, **10**, 503 (1938).

6. D. M. DENNISON, "A Theoretical Discussion," *Rev. Modern Phys.* **3**, 280 (1931).

7. W. W. COBLENTZ, "Investigations of Infra-red Spectra," *Pub.* 35, Carnegie Institute, 1905.

65. Raman Spectra.—When a cell containing a clear sample is placed in front of the slit of a spectrograph and is illuminated from the side by an intense beam of monochromatic light, the resulting spectrum shows three characteristics: (1) the presence
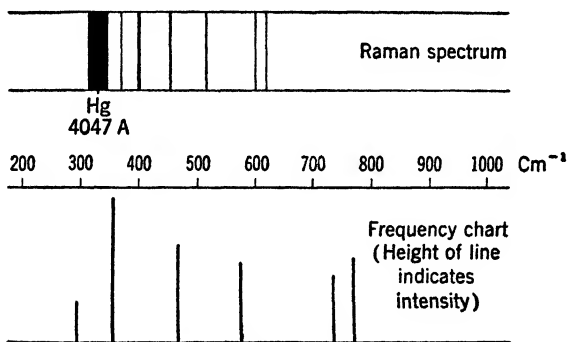
FIG. 95.

of the spectral line of the monochromatic source which has been scattered and reflected through the slit, (2) a faint continuous background due to a variety of factors including the fluorescence of the sample, and (3) the appearance of a very faint set of lines predominantly on the long wave-length side of the monochromatic exciting line (Fig. 95). This pattern of faint lines is called the Raman spectrum after Sir C. V. Raman, who discovered the effect in 1928. The difference between the frequency ν_e of the exciting line and the frequency ν_r of a Raman line is called the Raman frequency $\nu = \nu_e - \nu_r$. The Raman frequencies are, like infrared absorption bands, characteristic of the molecule and of various groups and linkages in the molecule.[66] As may be seen from Table 8, the Raman frequency of a given group or linkage may vary between narrow limits according to the nature of the rest of the molecule. Although the greatest use of Raman

spectra is as a method for elucidating the structure of molecules, some qualitative analytical procedures have been described.[67,68,69]

TABLE 8.—RAMAN FREQUENCIES OF A FEW SELECTED GROUPS

Group	Shift, cm.$^{-1}$
$\diagdown$C—H aliphatic	2,920–2,970
$\diagdown$C—H aromatic	3,054
—C—C— aliphatic	800– 860
—C—C— aromatic	1,580–1,608
—C=C—	1,600–1,650
$\diagdown$C—OH	820– 880
$\diagdown$C=O (carbonyl)	1,710–1,720
—C$\diagup$^{O} (acid)	1,654
$\diagdown$C—Cl	650– 710
$\diagdown$C—Br	570– 600

As an analytical method, Raman spectroscopy leaves much to be desired. However, it is applicable to the study of complex
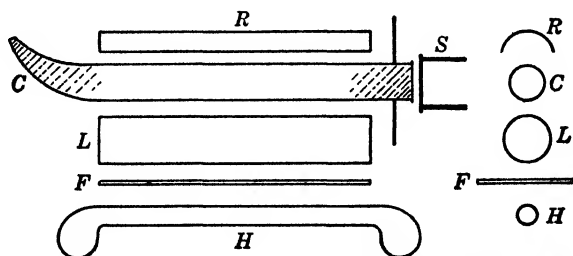
FIG. 96.—Raman cell and illuminator. (*After Wood.*[2])
R = ellipto-cylindrical reflector
C = Raman cell blackened on shaded parts
L = glass tube for liquid filter (*e.g.*, sodium nitrate solution)
F = glass filter to supplement L for isolation of single line
H = mercury vapor arc in air-cooled box
S = spectrograph

mixtures such as hydrocarbon distillates which can neither be separated nor analyzed effectively by chemical means. The dis-

advantages of the Raman method are that it requires about 10 ml. of fairly pure material for purposes of identification, it requires either a special spectrograph of high light-gathering power, or else exposures ranging up to several hours, and it is not applicable in many cases where the sample fluoresces or absorbs the Raman wave lengths. A common form of the Raman tube and illuminator is shown in Fig. 96.

Brode and Leermakers give a brief but excellent discussion of Raman spectroscopy in Gilman's text.[70] One of the recent comprehensive books on the subject is that of Hibben.[71] Griffiths *et al.* give a brief but complete summary of applications.[75]

SIMPLIFIED THEORY OF ABSORPTION SPECTRA

66. An atom may absorb energy in the form of heat or light by converting the incident energy into a form of potential energy. This is accomplished, as we have seen (Sec. 5), by an electron "jumping" from a low-energy level to a higher energy level. Thus, if a tube containing relatively cool sodium vapor is placed in front of a source of a continuous spectrum, the atoms of sodium will absorb certain discrete amounts of the radiant energy passing through them and be raised to an excited state. The absorption of energy must take place by a mechanism exactly the reverse of that involved in the emission of energy, *viz.*, by an electron jumping from a low-energy level to a higher energy level. Since the energy change $E_n - E_m$ must be the same as that involved in emission, then $E_n - E_m = h\nu_a = h\nu_e$ whence $\nu_a = \nu_e$. The subscripts a and e refer to absorption and emission, respectively. In other words, a cool atomic vapor is capable of absorbing certain of the frequencies that it emits when incandescent. In view of the fact that the cool vapor will not be in an initially high state of excitation, it follows that energy changes of a high order will be unlikely, *e.g.*, $E_{12} - E_{11}$. As a matter of fact, absorption in general is strongest for the resonance frequency corresponding to the electron jump from the ground state E_o to the first excited state E_1 or other low-energy levels E_2, E_3, etc. Thus the absorption spectrum of an atomic vapor will usually consist of a few dark lines due solely to electron jumps from a low-energy level to a slightly higher energy level.

In the case of a molecular vapor, however, there exist three means whereby discrete amounts of energy may be absorbed.

The first is similar to that already considered, *viz.*, an electron jump from a state of low energy to one of higher energy. In a molecule, however, the possible electronic energy levels are modified by the presence of several atoms. A molecule may also absorb energy by converting it into energy of *vibration*. In a dumbbell-shaped diatomic molecule, this vibration will be linear and analogous to that of two bodies connected by a spring. Further, a molecule may absorb energy by converting it into *rotational energy* or into a combination of rotational and vibrational energy. In general, the energy involved in an electron jump will be greater than that involved in vibration or rotation. It must be remembered that in accordance with the fundamental law of Planck all these energy changes are discrete or quantized.

It is now possible to write an equation expressing the absorption of light by a molecule

$$h\nu = (E_{l1} - E_{L2}) + (E_{Vn} - E_{Vm}) + (E_{Rn} - E_{Rm})$$

The subscripts refer to electronic, vibrational, and rotational discrete energy changes. Thus an absorption line corresponding to a single electronic energy change $E_{I1} - E_{E2}$ is found to be spread out into a band of many fine lines because of the many possible values of $E_{Vn} - E_{Vm}$ and $E_{Rn} - E_{Rm}$. In other words, the frequency ν may take on a large number of values for any one electron jump, although these values will all be in the vicinity of the frequency ν_e predicted by

$$E_{E1} - E_{E2} = h\nu_e$$

This state of affairs holds true in general for a molecular vapor or gas. If this gas is compressed, however, it is observed that the fine lines of the band spectrum coalesce because of the effects of crowding the molecules together. Finally, in a liquid all the fine structure will become simply a *region* of absorption. Such an absorption region may represent only a single electron transition, modified by vibrational and rotational effects.

Infrared and Raman spectra usually involve energy transitions due to vibration and rotation alone, *i.e.*, no electronic transition is necessary. It is thus possible to study the dynamics of the molecule itself.

67. Experimental.—Owing to the diversity of types, it is not considered feasible to go into the details of the adjustments of

each instrument. Brode,[5] Twyman and Alsopp,[11] and Miller[9] describe the procedure of adjustment for several instruments, but usually the manufacturer's pamphlet of directions gives sufficiently detailed instructions. The spectroscopic part of the instrument may be adjusted in accordance with directions given in Secs. 51 and 52. It is highly important that the source be placed precisely on the optical axis of the instrument and that the cells and cell holder be aligned so that each cell receives the same amount of light.

The Wedge Spectroscope.—Given a solution of uranine, iodobenzoin, rose bengal 5B, potassium permanganate, janus green, or chromium diphenylcarbazide, place the solution in the cell and examine the absorption curve. Make a rough sketch of same, indicating the wave length of all maxima and minima. The solution may be diluted if necessary, and then diluted progressively until the last band disappears. Sketches of the curve should be made at each recorded concentration.

Photoelectric Spectrophotometer 350 *to* 750 $M\mu$.—The instrument is adjusted according to the directions of the manufacturer, supplemented by the information given in Secs. 51 and 52. The instrument may then be checked by determining the transmission curve of a didymium glass filter whose transmission has been measured by the Bureau of Standards,[72] or of a molar solution of potassium chromate in 0.05N aqueous potassium hydroxide.[12]

One of the solutions used in the preceding experiment is placed in a previously cleaned and dried cell (Sec. 53), and an identical cell is filled with solvent. If necessary, the solutions are first filtered through the finest grade of sintered glass. The outer walls are wiped clean with lintless cloth or bibulous paper and placed in their proper positions in the instrument. The previously aligned light source is started and allowed to come to equilibrium, during which time the entrance and exit slits are set to their proper widths, which are determined by the complexity of the curve as observed with the wedge spectroscope. The cells are reexamined for the presence of bubbles, and the steadiness of the source is checked by observing the constancy of the galvanometer deflection. Transmission values are then determined at wave-length intervals whose spacing depends on the slit width and on the complexity or steepness of the absorption curve. Over gently sloping portions of the curve, only a

few transmission measurements are necessary, but when the curve slopes sharply, or where there is an inflection, as many readings as possible are taken.   It is usually necessary to make all wave-length settings in the same direction to avoid backlash in the mechanism.   When the curve is finished, several points are rechecked to give the error of the setting and to show the presence or absence of photochemical effects.   The cells are removed, cleaned, and refilled with solvent and a solution of widely different concentration.   A second curve is constructed, and the specific extinction k or molecular extinction ϵ, or $E_{1\,cm.}^{1\%}$ is calculated at a suitable transmission minimum.   If the specific extinctions differ appreciably, a third curve or portion of a curve is constructed at an intermediate concentration and a third value of k, ϵ, or $E_{1\,cm.}^{1\%}$ is calculated.   A curve is constructed of log (I_o/I) or K vs. concentration, which expresses the deviation from Beer's law at the wave length chosen.   A solution of unknown concentration is then placed in the cell, and its concentration is determined either from the known constant value of k, ϵ, or $E_{1\,cm.}^{1\%}$ or from the plot of K vs. c.

The Ultraviolet Spectrophotometer—Photographic.—One of the most practical experiments is the determination of the potency of vitamin A preparations by measuring $E_{1\,cm.}^{1\%}$ at the characteristic transmission minimum at 328 mμ.   The potency in international vitamin A units is 2,200 $E_{1\,cm.}^{1\%}$.   Cod-liver oil is a readily available source.

Solutions of benzene in alcohol give a rather complicated curve showing five steep minima.   Brode[5] gives complete directions for these experiments and a good bibliography.

PROBLEMS

1. At a given wave length, a solution of 0.01 mg./ml. of a certain substance shows a transmission of 15 per cent in a 1-cm. cell.

a. What will be the transmission of the solution in a 2-cm. cell?

b. What will be the transmission of a solution having twice the concentration?

c. If the molecular weight is 142, calculate ϵ.

2. A 4 cm. thickness of a solution of unknown concentration is found to show the same transmission as a 1 cm. thickness of a solution containing 0.003 mg./ml. of the same solute, the same wave length of minimum transmission being used in each case.   What is the concentration of the unknown solution?

3. A pure sample of oil shows a transmission of 40 per cent at 3,400 A in a 2-cm. cell. What is the extinction coefficient? Will this value necessarily hold for solutions of the oil in an inert solvent?

4. *a.* If a colored liquid shows a strong absorption band between 400 and 600 f, what might be its color?

    b. Do all colored solutions necessarily show absorption in the visible region?

    c. If a liquid absorbs strongly in the region 4,900 to 6,000 A and transmits all other wave lengths freely, what is its appearance?

5. It is a common property of solutions of certain substances to change color on dilution. Enumerate some of the possible reasons for such a phenomenon. Which of the phenomena will not occur in nonpolar completely inert solvents?

6. Make a tabular summary of the relative merits and disadvantages of visual, photoelectric, and photographic spectrophotometers. Choose as representative examples, the Hilger-Nutting, Cenco, and Spekker instruments.

7. List the factors affecting the experimental determination of transmission with a visual spectrophotometer and with the Spekker spectrophotometer (compare with the list in Sec. 50).

8. Will the stray light error be greater in general for large or small transmission values?

9. If the entrance slit of the Coleman spectrophotometer subtends a band 5 mμ wide on the exit slit, what will be the net effective width of the monochromatic band passed by an exit slit of 2, 5, and 10 mμ effective width? What will be the half-intensity width H?

10. The following data are obtained for a solution of 1.000 g./liter of a biological pigment in chloroform. The cell length is 1.00 cm., and the effective slit width is 3 mμ.

λ	% T	λ	% T	λ	% T
450	93.0	540	42.1	620	80.2
460	86.5	545	43.5	630	82.1
470	77.0	550	47.3	640	84.8
480	62.5	555	48.0	650	86.2
490	52.0	560	48.6	660	88.0
500	36.0	565	49.2	670	89.6
505	32.1	570	51.4	680	90.4
510	30.0	575	58.0	690	91.2
515	29.1	580	64.1	700	90.9
520	29.2	590	70.0	710	90.1
525	29.9	600	74.1	720	89.2
530	32.0	610	77.0	730	87.3

    a. Plot the percentage transmission curve vs. wave length from left to right.

    b. Plot k vs. frequency from left to right.

11. The curves shown in Fig. 97 have been constructed from data on aqueous dye solutions of varying concentration.   The same solvent, solute
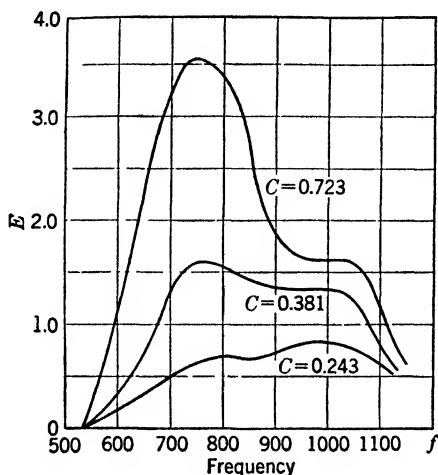

Fig. 97.

cell, and instrument have been used throughout, and the instrument setting has remained the same.

   a. What might account for the observed effect of dilution?

   b. Would the solution obey Beer's law at 715 f?

   c. If the extinction values were measured only at the peaks of the curve, would you expect Beer's law to be obeyed?

12. *a.* A sample of solution gives a transmission of 24.2 per cent with reference to a cell containing solvent.   When the cells are exchanged, the transmission becomes 24.4 per cent.   What is the true value?

   b. On rechecking the transmission of the same sample in the first cell, it is found to be 24.8 per cent, although the instrument has not been altered. What reasons could you suggest for this variation?

   c. If the width of the exit slit is doubled, the transmission of the same sample becomes 31.2 per cent, but if the exit slit is narrowed to half its original width, the observed transmission is 20.4 per cent.   Explain.

13. Why is infrared spectrophotometry of importance in analytical work when the experimental procedure is so much more complicated than visual and ultraviolet methods?

14. The following data were obtained by means of a photoelectric spectrophotometer using a 2 mμ effective slit width and a 2.00-cm. cell.   The solvent is iso-octane, the wave length 310 mμ.

c, g./liter	% T
0.0105	44.8
0.0210	20.0
0.0280	11.7

a. Plot E vs. concentration. Does the solution obey Beer's law within the experimental limits of 1 per cent?

b. What is the average value of the specific extinction?

c. What is the concentration of a solution that shows a transmission of 28.7 per cent in a 2-cm. cell?   A transmission of 52.4 per cent in a 1-cm. cell?

REFERENCES

1. A. C. HARDY, "Handbook of Color Analysis," Technology Press, Massachusetts Institute of Technology, Cambridge, Mass., 1936.
2. K. S. GIBSON *et al.*, *J. Optical Soc. Am*, **10**, 169 (1925).
3. J. H. YOE, "Photometric Chemical Analysis," Vol. I, John Wiley & Sons, Inc., New York, 1928.
4. F. D. SNELL and C. T. SNELL, "Colorimetric Methods of Analysis," D. Van Nostrand, Company, Inc., New York, 1936.
5. W. R. BRODE, "Chemical Spectroscopy," John Wiley & Sons, Inc., New York, 1939.
6. R. A. MORTON, "Absorption Spectra of Vitamins and Hormones," A. Hilger, London, 1935.
7. F. TWYMAN, "The Practice of Absorption Spectrophotometry," A. Hilger, London, 1932.
8. O. J. WALKER, "Absorption Spectrophotometry and Its Applications," A. Hilger, London, 1939.
9. E. S. MILLER, "Quantitative Biological Spectroscopy," Burgess Publishing Co., Minneapolis, 1939.
10. A. BEER, *Ann. der Physik. Chemie* (Poggendorff), (3), **26**, 78 (1852).
11. F. TWYMAN and C. B. ALSOPP, "The Practice of Absorption Spectrophotometry with Hilger Instruments," A. Hilger, London, 1934.
12. T. R. HOGNESS, Z. P. ZSCHEILE, and A. E. SIDWELL, *J. Phys. Chem*, **41**, 379 (1937).
13. S. E. Q. ASHLEY, *Ind. Eng. Chem. Anal. Ed.*, **11**, 379 (1937).
14. J. W. T. WALSH, "Photometry," Constable & Company, Ltd., London, 1926.
15. W. BÖTTGER, "Physikalische Methoden der Analytischen Chemie," Akad. Verlagsgesellschaft, Leipzig, 1939.
16. L. C. MARTIN, "Optical Measuring Instruments," Blackie & Son, Ltd., Glasgow, 1924.
17. V. K. ZWORYKIN and E. D. WILSON, "Photocells and Their Applications," John Wiley & Sons, Inc., New York, 1934.
18. R. P. WITHROW, C. S. SHREWESBURY, and H. R. KRAYBILL, *Ind. Eng. Chem. Anal. Ed.*, **8**, 214 (1936).
19. R. H. MÜLLER, *ibid.*, **11**, 1 (1939).
20. H. M. PARTRIDGE, *ibid.*, **2**, 207 (1930).
21. C. J. BARTON and J. H. YOE, *ibid.*, **12**, 167 (1940).
22. F. LOEWENBERG, U. S. Pat. 2034334.
23. G. LANGE, "Photoelemente und Ihre Anwendung," J. A. Barth, Leipzig, 1936.

24. J. STRONG, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, 1938.
25. F. S. BRACKETT and E. D. MCALISTER, *Rev. Sci. Instruments*, **1**, 191 (1930).
26. P. K. SESCHEN, *J. Sci. Instruments*, **12**, 261 (1935).
27. H. C. UREY *et al.*, *Rev. Sci. Instruments*, **3**, 497 (1932).
28. A. J. ALLEN, *J. Optical Soc. Am.*, **31**, 268 (1941).
29. J. S. PRESTON, *J. Sci. Instruments*, **13**, 368 (1936).
30. O. W. PINEO, *J. Optical Soc. Am.*, **30**, 276 (1940).
31. J. L. MICHAELSON, *J. Optical Soc. Am.*, **8**, 365 (1938).
32. G. R. HARRISON *et al.*, "Proceedings of the Sixth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1939; *J. Optical Soc. Am.*, **30**, 290 (1940).
33. W. DECK, *Helvetica Phys. Acta*, **11**, 3 (1938).
34. S. JACOBSEN, H. E. BENT, and A. J. HARRISON, *Rev. Sci. Instruments*, **11**, 221 (1940).
35. K. S. GIBSON, *J. Opt. Soc. Am.*, **24**, 234 (1934).
36. H. VON HALBAN and H. GIEGEL, *Z. physik. Chem.*, **96**, 214 (1920).
37. H. VON HALBAN and K. SIEDENTOPF, *ibid.*, **100**, 208 (1922).
38. N. WRIGHT, *Ind. Eng. Chem. Anal. Ed.*, **13**, 1 (1941).
39. O. E. MILLER, *Rev. Sci. Instruments*, **3**, 30 (1932).
40. D. L. DRABKIN, "Proceedings of the Seventh Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1940.
41. Optical Society of America Progress Committee, *J. Optical Soc. Am.*, **10**, 169 (1925).
42. C. E. K. MEES and S. H. WALKER, *Brit. J. Phot.*, **54**, 384 (1907).
43. J. W. NICHOLSEN and T. R. MERTON, *Trans. Roy. Soc. (London) A*, **216**, 459 (1916).
44. E. GOLDBERG, *Brit. J. Phot.*, **57**, 648 (1910).
45. D. H. FOLLETT, *J. Sci. Instruments*, **13**, 221 (1936).
46. D. L. DRABKIN, "Proceedings of the Fifth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1938.
47. B. O'BRIEN, "Proceedings of the Sixth Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1939.
48. E. R. HOLIDAY, *J. Sci. Instruments*, **44**, 166 (1937).
49. J. H. MOLL, H. C. BURGER, and W. G. REICHERT, *J. Sci. Instruments*, **7**, 148 (1935).
50. E. C. C. BALY, "Spectroscopy," Longmanns, Green & Company, New York, 1927.
51. J. S. OWENS, "Proceedings of the Seventh Summer Conference on Spectroscopy and Its Applications," John Wiley & Sons, Inc., New York, 1940.
52. W. E. RUEHLE and E. K. JAYCOX, *ibid.*, p. 10.

53. F. Twyman, L. J. Spencer, and A. Harvey, *Trans. Optical Soc. (London)*, 33 (1931–1932).

54. R. Twyman, *Proc. Phys. Soc. (London)*, **45**, 1 (1933).

55. A. J. Allen, *J. Optical Soc. Am.*, **31**, 268 (1941).

56. P. K. Seshan, *J. Sci. Instruments*, **12**, 261 (1935).

57. H. J. McNicholas, *Bur. Standards Research Paper*, **1**, 939 (1928).

58. W. C. Holmes and J. T. Scanlan, *U. S. Dept. Agric. Tech. Bull.* 310 (1932).

59. W. M. Murray and S. E. Q. Ashley, *Ind. Eng. Chem. Anal. Ed.*, **10**, 1 (1938).

60. F. Weigert, *Ber.*, **49**, 1529 (1916).

61. R. Twyman and G. F. Lothian, *Proc. Roy. Phys. Soc. (London)*, **45**, 643 (1933).

62. M. Barnard and P. McMichael, *Ind. Eng. Chem. Anal. Ed.*, **2**, 363 (1930).

63. H. W. Knudsen, *Ind. Eng. Chem. Anal. Ed.*, **12**, 715 (1940).

64. E. B. Moss, *J. Sci. Instruments*, **12**, 5 (1935).

65. L. W. Gildart and N. Wright, *Rev. Sci. Instruments*, **12**, 204 (1941).

66. J. H. Hibben, *Chem. Rev.*, **13**, 1 (1936).

67. E. A. Crigler, *J. Am. Chem. Soc.*, **54**, 4207 (1932).

68. J. Goubeau, *Z. anal. Chem.*, **105**, 161 (1936).

69. A. V. Grosse, E. J. Rosenbaum, and H. F. Jacobson, *Ind. Eng. Chem. Anal. Ed.*, **12**, 191 (1940).

70. H. Gilman, "Organic Chemistry," John Wiley & Sons, Inc., New York, 1938.

71. J. H. Hibben, "The Raman Effect and Its Chemical Applications," Reinhold Publishing Corporation, New York, 1939.

72. K. S. Gibson, G. K. Walker, and M. E. Brown, *J. Optical Soc. Am.*, **24**, 58 (1939).

73. Coleman Electric Company, "The Relative Accuracy of the Coleman Model 10-S Double Monochromator Spectrophotometer," Maywood, Illinois, 1940.

74. H. J. McNicholas, *U. S. Bur. Standards Research Paper*, 30 (1928).

75. J. G. A. Griffiths, H. C. Gull, and H. K. Whalley, *Ann. Repts. Chem. Soc. (London)*, **35**, 395 (1938).

76. H. J. Reich, "Theory and Application of Electron Tubes," McGraw-Hill Book Company, Inc., New York, 1939.

77. K. S. Gibson, *J. Opt. Soc. Am.* **21**, 564 (1931).

CHAPTER III

THE COLORIMETER, TURBIDIMETER, NEPHELOMETER, AND FLUOROPHOTOMETER

68. The four instruments discussed in this chapter all depend on the measurement of the intensity of light transmitted, reflected, or produced through fluorescence by particles suspended in a liquid. The particles may be molecules, colloidal aggregates of molecules, or even somewhat larger particles, but in all cases their concentration must govern the magnitude of the observed effect.

The colorimeter is an instrument for measuring the transmission of a clear, colored solution relative to that of a reference standard, whereas the turbidimeter is an analogous instrument employed for the special case of turbid suspensions that may or may not be classed as colloids. The nephelometer, or Tyndallmeter, on the other hand, is an instrument designed to measure the amount of light scattered by suspended particles illuminated laterally by an intense beam of white or monochromatic light. The fluorophotometer, or fluorimeter, is similar in design, but the light observed is produced by fluorescence rather than by scattering. The lateral illuminating beam is usually ultraviolet, and the method is applicable only to those substances that fluoresce quite strongly.

All four instruments are widely used in chemical analysis, especially in industrial testing laboratories where the speed and simplicity of the methods are particularly important. The colorimeter, which is undoubtedly the most popular of the four, is recommended as a quantitative method whose speed and precision are second to no other method of comparable range, and whose sensitivity is second only to that of the spectrograph. The method is very general, and procedures have been developed for the quantitative determination of nearly every known element, with the exception of the rare gases and certain of the rare earths. The method is also applicable to radicals and organic groups and is much used in biochemistry and clinical analysis. The turbidimeter is used principally for sulfur analysis

and for the analysis of sulfates in boiler water, whereas the nephelometer is employed in checking the clarity of commercial filtrates and beverages. Although the fluorophotometer is a relatively new instrument, it is already used extensively in vitamin assay work and in a number of other specialized fields.

THE COLORIMETER

69. In order to talk intelligently about color and its measurement, it is necessary to define certain terms in an unambiguous way, especially since the chemist and physicist often understand different meanings for the same term. In this discussion, the following definitions only will apply:

Chemical colorimetry or colorimetric analysis implies the determination of the concentration of a colored solute by measurement of the relative absorption or transmission of the solution.

Brightness (brilliance) "is that attribute of any color in respect of which it may be classed as equivalent to some member of a series of grays ranging from white to black." Brightness is practically synonymous with "transmitted intensity" and is roughly inversely proportional to the concentration of a colored solution.

Hue is that attribute which distinguishes a color as reddish, yellowish, greenish, etc.

Purity (saturation or chroma) denotes the degree of redness, yellowness, greenness, etc.

Other terms which are used below have been defined in the preceding chapter. Those used in connection with Beer's law are restated here for the sake of convenience:

Beer-Lambert law:

$$\log_{10}\left(\frac{I_o}{I}\right) = kcl$$

where I_o/I is the ratio of the intensity of the incident to the transmitted light that passes through l cm. of a solution whose concentration c of colored solute is expressed in grams per liter, or milligrams per milliliter. The constant k is called the specific extinction and is characteristic of the solute. The ratio I/I_o is called the transmission T.

When the lengths of the columns of two solutions of the same solute having different concentrations are so adjusted that their

transmissions are equal, then

$$\log_{10}\left(\frac{I_{o1}}{I_1}\right) = \log_{10}\left(\frac{I_{o2}}{I_2}\right) = kc_1l_1 = kc_2l_2$$

whence

$$c_1l_1 = c_2l_2 \quad \text{or} \quad \frac{c_1}{c_2} = \frac{l_2}{l_1}$$

This simple proportion is also usually called Beer's law and is the basic principle of chemical colorimetry. Deviations from Beer's law have been mentioned in Sec. 45 and will be referred to in detail in Sec. 74.

70. Dilution Methods and Use of a Series of Standards.— These methods are used for quantitative comparison between
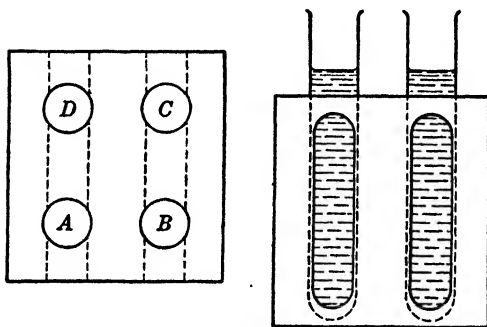
Fig. 98.—The Walpole comparator.
A = standard solution and color producing reagent
B = unknown solution and color producing reagent
C = pure solvent plus color producing reagent
D = unknown solution plus water

two solutions, the apparatus consisting of two identical test tubes, or identical graduated Nessler, Eggertz, or Julian tubes, and suitable volumetric equipment. The solution of unknown concentration is placed in one tube, and a measured volume of a stronger solution of known concentration is placed in the other test tube. The latter solution is then diluted with a measured amount of solvent until the brightness equals that of the unknown solution when the two tubes are viewed from the side. The concentrations will then be equal, and that of the unknown is easily computed.

The various dilutions of standard may, of course, be made up permanently from matching mineral colors or fast dyes which

are sealed in test tubes and arranged in a series according to the concentrations they represent. No color standard is truly permanent, however, and the sealed test tubes should be stored in a cool place in absolute darkness.

An alternative method is to dilute progressively the unknown solution until it matches a standard solution, which may well be a permanent sealed standard of the type mentioned above.

The four- or six-tube comparator (Fig. 98) is sometimes used when greater visual accuracy is required. The second bank of holes (*D*, *C*) permits the use of tubes which compensate for any extraneous hue present in the sample. This principle, first described by Walpole, is illustrated in the figure, the assumption being that it is desired to measure the amount of copper by the ammonia method in a solution which has a faint yellow tint. A measured excess of concentrated ammonia is added to the sample *B* and to the standard copper solution *A*, but the two tubes will not appear of exactly the same hue because of the yellow component in the sample. It is possible, however, to place the faint yellow sample in tube *D* and add an amount of water equal to the volume of ammonia added to *B*, so that there will be as much yellow in the left-hand optical path as in the right-hand path. The tube of pure water or dilute ammonia *C* compensates for the added thickness of cell *D*.

FIG. 99.— Nessler tubes. (*Courtesy of Central Scientific Company.*)

For very dilute solutions, it is necessary to use a liquid thickness greater than that furnished by the diameter of test tubes. In such cases, it is customary to employ Nessler
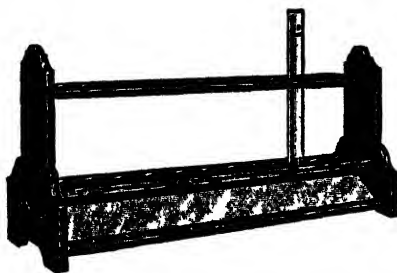
FIG. 100.—Nessler tube holder. (*Courtesy of Central Scientific Company.*)

tubes (Fig. 99). These are very carefully matched in capacity, and a mark is made at a certain height from the bottom. The tubes are suspended in a holder similar to that shown in Fig. 100 and filled exactly to the mark with the colored solutions. The

optical device shown in Figs. 101 and 102 permits viewing a split field, which increases the accuracy somewhat.[1]
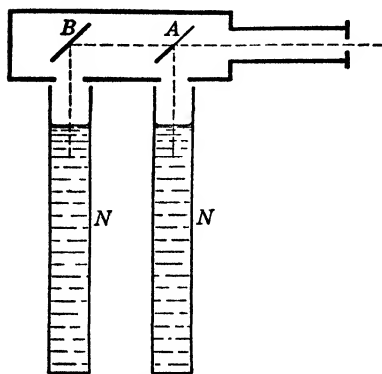
FIG. 101.—Nessler tube colorimeter.
A = half-silvered mirror
B = mirror
NN = Nessler tubes

In both dilution procedures, the calculations are carried out by the proportion

$$\frac{\text{Concentration of sample}}{\text{Concentration of standard}}$$
$$= \frac{\text{volume of sample}}{\text{volume of standard}}$$

No calculations are required for the method of permanent standards except when an interpolation is advisable.

Colored glass standards are popular in certain specialized fields such as pH determination.[2] One of the better types of comparator is shown in Fig. 103. Although the glass standards are expensive, they are sufficiently superior to liquid standards
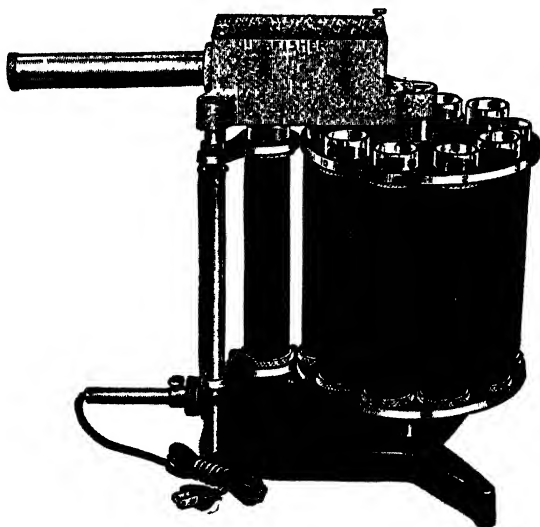
FIG. 102.—The Fisher Nesslerimeter. (*Courtesy of Fisher Scientific Company.*)

to warrant the additional cost when comparisons are to be made over a long period of time.

The Lovibond tintometer,[3] shown in Fig. 104, is still used to some extent for color control in the oil and food industries.   Any color may be matched by the use of three or four superposed and numbered colored glasses from an extensive series, and the hue may be described in terms of the numbers.
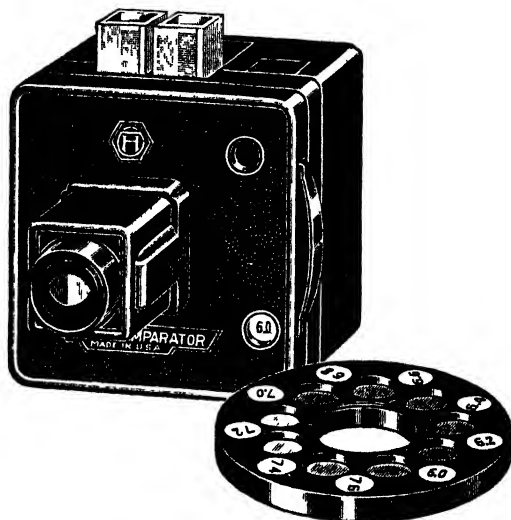
Fig. 103.—Hellige comparator.   (*Courtesy of Hellige Inc.*)
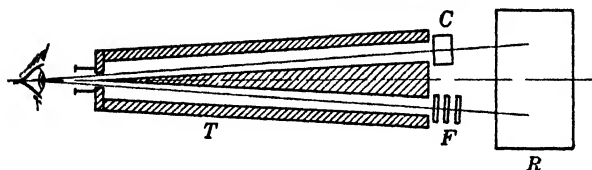
Fig. 104.—The Lovibond tintometer.
T = frame made of wood with optical black finish
C = cell containing liquid
F = comparison plates of colored glass
R = diffuse reflector

71. The Nessler Tube, Hehner Tube, and Related Methods.—
It follows from Beer's law that the optical length of a column of solution can be varied until its transmission equals that of a known length of standard when the proportion $c_1:c_2 = l_2:l_1$ applies.   This procedure is obviously far easier to carry out than the dilution methods discussed above and is capable of greater refinements.

Before going into this topic, however, two of the less elaborate methods will be described because of their wide use in industrial testing laboratories. The principle upon which these methods depend is most easily illustrated in the case of the Hehner tube colorimeter shown in Fig. 105. The unknown sample is placed in one tube and the standard in an identical tube. The heights of the two solutions are then adjusted until the brightnesses appear equal when the tubes are placed vertically over a diffuse illumination and viewed from the top. Graduations on the side of each tube give the height of each column, and the unknown concentration is calcu-
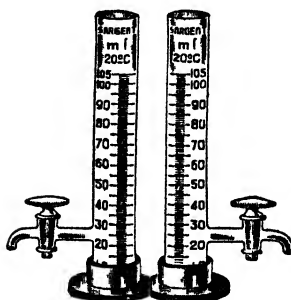
Fig. 105.—Hehner tubes. (*Courtesy of E. H. Sargent & Company.*)
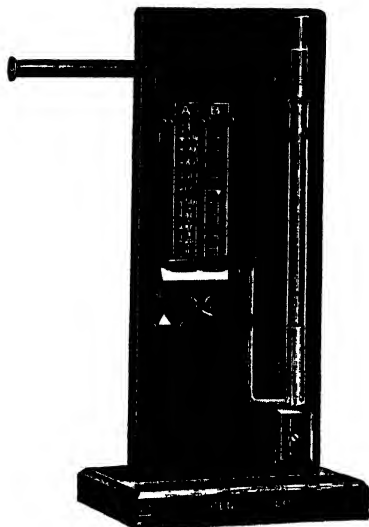
Fig. 106.—The Campbell-Hurley colorimeter. (*Courtesy of Central Scientific Company.*)

lated by the simple Beer's law proportion. An improved comparator operating on the same principle is shown in Fig. 106. These devices all require a considerable volume of solution, but owing to the large depth, very small concentrations may be determined with an accuracy of the order of 5 per cent.

72. The Duboscq Colorimeter and Allied Instruments.—The operation of the Duboscq colorimeter is shown schematically in Fig. 107. By raising or lowering the glass plungers, the brightness of the two halves of the split field may be matched with great accuracy. A scale shows the height of each column of liquid in millimeters and tenths. This type of colorimeter is probably more generally used than any other precision instrument and is capable of much greater accuracy than is generally

supposed.   Under usual laboratory conditions, successive scale readings should not deviate by more than about 3 per cent, provided that the operator is experienced and the color of the solution is within the yellow-green region of maximum visual sensitivity.

The Duboscq instrument is usually equipped with the millimeter scale mentioned above and with cups whose capacity varies from about 15 to 25 ml.   A great many modifications are on the market, however, designed for special purposes (Figs. 108 and 110).   The micro colorimeter, shown in Fig. 108, operates on the principle of the Campbell-Hurley instrument (Fig. 106).   It is also possible to employ micro cups and tubes for standard size Duboscq instruments.   Some of the recent colorimeters have a scale

FIG. 107.—D u b o s c q colorimeter (simplified).

E = magnifying eyepiece
RR = comparison rhombs
CC = cups mounted on rack-and-pinion device
M = mirror
PP = plungers

FIG. 108.—Micro colorimeter. (*Sheftel.*) (*Courtesy of Fisher Scientific Company.*)

reading directly the ratio of sample to standard (Figs. 109 and 110).   Other modified Duboscq models are equipped with deeper cups for observing faint colors, and still others have water-cooled cups for constant-temperature work. Yoe[4] and Snell and Snell[5] describe many such instruments, but descriptions of very recent models are available only in the manufacturers' catalogues.

To ensure uniformity of illumination, it is best to employ artificial light filtered through blue ground glass. A Chalet lamp
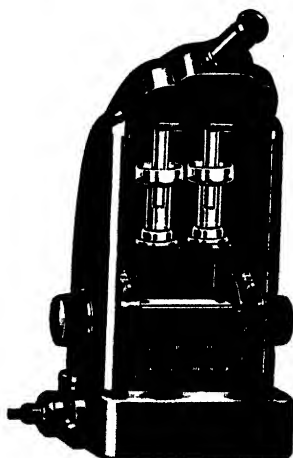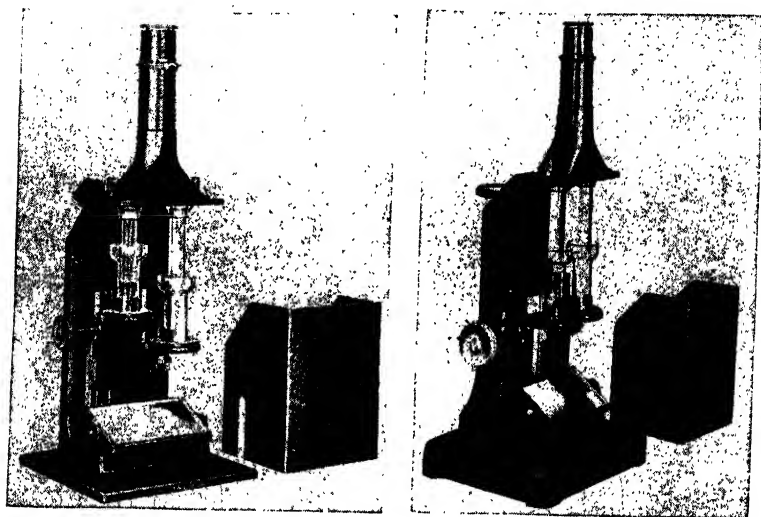
Fig. 109.—Duboscq colorimeters. (*Courtesy of Bausch & Lomb Optical Company and Hellige, Inc.*)

of the type described in Sec. 116 is recommended only if the window measurement is larger than about 3 by 4 in., but the

special illuminators now on the market present some advantages (Fig. 111).

FIG 110 —Spencer drum-scale Duboscq colorimeter   (*Courtesy of Central Scientific Company, Spencer Lens Company*)
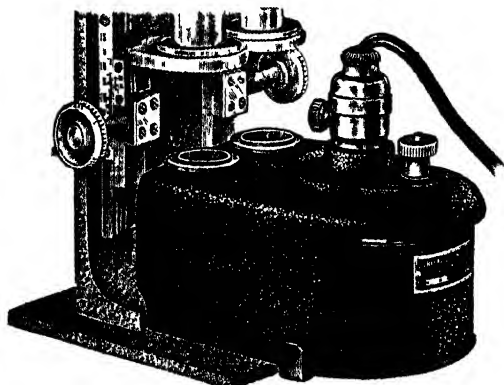
FIG. 111 —Colorimeter illuminator   (*Courtesy of Bausch & Lomb Optical Company*)

Since Beer's law cannot be followed exactly unless monochromatic light is employed, and since the absorption of a solution may be increased by using a filter of complementary hue, it

is nearly always advisable to use such a filter. Armstrong[6] claims that a very appreciable increase in accuracy results from the use of filters (see also Wirth[7]).

Whatever type of Duboscq instrument is used, it should be treated with all the care that a delicate optical device deserves. The glass parts should be free of all internal flaws and must be optically perfect. Great care must be taken to clean the cups and plungers after use, and it is usually necessary to brush the upper surface of the twin rhombs to remove any dust. The moving parts should be free from backlash, and the scale should be adjusted to read zero when the plunger just touches the bottom of the cup. Obviously, the two halves of the field must match when the cups are empty, and the dividing line between them should be nearly invisible.

73. Use of the Duboscq Colorimeter.—The following directions are given in "cook-book" style for the sake of brevity, since the reasons for each step will be considered in due course.

Rinse both of the clean cups with the sample solution, and fill about half full. The right-hand scale is then set at 20.0 mm. exactly (or at any other convenient reading S), and the left-hand cup is moved up or down until the two halves of the field match. This setting should be repeated ten times, the approach being made alternately from the top and bottom, and the readings are then averaged. Set the left-hand scale at this reading. The solution in the right-hand cup is then discarded, the cup and plunger are rinsed with standard solution, and the cup is half-filled with standard solution. The right-hand cup is then moved up and down until a match is observed. Ten readings are averaged as before, and the average is denoted by Y. To check on the validity of Beer's law for the sample used, the standard solution in the right-hand cup is then removed and diluted to precisely two-thirds of its original concentration. It is replaced in the rinsed right-hand cup. The latter is again adjusted to the match point and the average of 10 settings taken as Y'. The two solutions are then discarded and the cups cleaned and dried.

The preceding method automatically eliminates any scale error, since the left-hand side functions only as a fixed reference. The extent of any deviation from Beer's law may be estimated from the dilution results. Obviously if $Y' = \frac{3}{2}Y$, Beer's law

holds, and the calculation reduces to $c = (Y/S)c_o$ where c is the concentration of the sample, c_o is the concentration of the standard, and S is the original left-hand setting (20 mm.). Yoe[4] and McCrackan et al.[8] give tables for calculating c when c_o and Y are known and the right-hand setting is 20 mm.

74. Deviations from Beer's law have already been discussed in Secs. 45 and 53, but no mention has been made of possible methods of compensation. Use of monochromatic filters some-times eliminates such devia-tions, since Beer's law is rarely followed when white light is used. It is always possible, of course, to construct a working curve from standards of known concentration. Most workers recommend plotting the Y reading referred to above against the known concentra-tion of a series of prepared samples, when a straight line is obtained (curve O in Fig. 112). Note that this line may be practically straight and still not coincide with the theoret-ical curve T predicted by Beer's law. This phenomenon
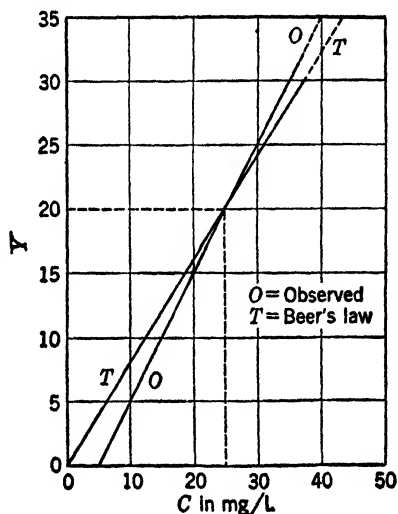
FIG. 112.

is often encountered and is doubtless due to one or more of the above-mentioned factors which are known to influence the concentration-transmission relationship.

Because of the need of a constant numerical factor to express the observed linear deviation from Beer's law, Yoe[4] has suggested the use of an equation originally developed by Kober

$$S = \frac{Y}{R} - \frac{(1 - R)YK}{R^2}$$

where $R = (C/C_o)$ and K, the so-called Kober's constant, is the desired factor. The Kober factor may be evaluated from the experimentally determined values Y and Y', referred to in the preceding section, by solution of two simultaneous equations. In this case, R' will equal $\frac{3}{2}R$, and c need not be known. The

two equations will be

$$S = \frac{Y}{R} - \frac{(1 - R)YK}{R^2}$$

$$S = \frac{Y'}{\tfrac{3}{2}R} - \frac{(1 - \tfrac{3}{2}R)Y'K}{(\tfrac{3}{2}R)^2}$$

where S, Y, and Y' are known. The equations may then be solved for R and K.

A mathematically simpler procedure is to determine Y when both c and c_o are known. Then, on rearranging the equation, we obtain

$$K = -\frac{R^2 S - RY}{(1 - R)Y}$$

where all terms on the right-hand side are known. The following example illustrates a typical calculation:

Let c = concentration of prepared sample = 0.0600 mg./ml.

$\quad c_o$ = concentration of reference standard = 0.0500 mg./ml.

$\quad S$ = depth of sample = 20 mm.

$\quad Y$ = depth of reference standard = 24.6 mm.

Then

$$R = \frac{c}{c_o} = 1.20$$

$$K = -\frac{(1.20)^2(20.0) - (1.20)24.6}{(1 - 1.20)24.6} = -0.14$$

The negative sign signifies that the actual working curve has a larger (steeper) slope than the curve predicted by Beer's law. This constant is characteristic of the solution in question and should be included in published work whenever it applies. It does not apply when c is less than $c_o/2$, nor when the concentration range is wide enough to cause the working curve to deviate greatly from linearity.

Winkler[9] and Ginsberg[10] have suggested that the simple Beer's law proportion be written in the form

$$\frac{(c_1 + k)}{(c_2 + k)} = \frac{l_2}{l_1} \qquad \cdot$$

where k is calculated from the difference between the actual and experimentally determined concentrations. This method is

not widely used, however, because k is not always a constant. (k does not refer to specific extinction.)

75. Wedge-cell colorimeters operate on the balancing principle of the Duboscq instrument, but the variations in depth are accomplished by using two hollow wedges filled with sample and standard, respectively. The vertical wedges (Fig. 113) are moved up and down in graduated carriers, and a narrow portion of each is viewed horizontally through a suitable comparison eyepiece. These instruments are capable of great accuracy
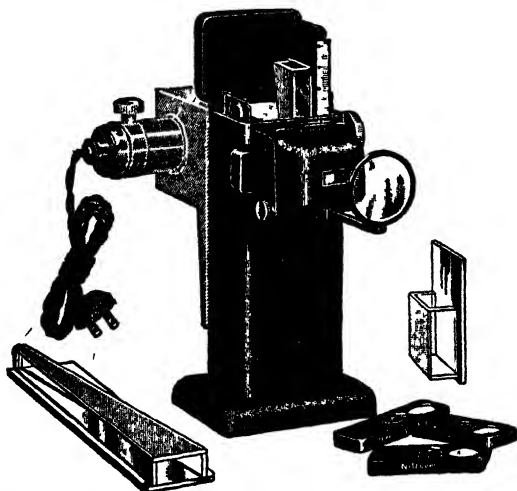
FIG. 113.—Wedge colorimeter.   (*Courtesy of Hellige, Inc.*)

and are especially useful for pH and biological work. Note that only one wedge is actually required and that the other may be replaced by a rectangular container.

76. Neutral-wedge and polarization photometers are generally regarded as the most accurate of the visual colorimeters, but they are subject to the limitations imposed by the use of filters. The neutral-wedge photometer,[11,12] shown in Fig. 114, employs a movable wedge of dark glass whose density gradient is linear. The sample, in a $\frac{1}{2}$- to 4-in. cell, is placed in one side of the optical path, and the thickness of the wedge is adjusted until the intensity of the two halves of the field is the same. It is obviously necessary that both halves of the field be of the same hue, and, to accomplish this, special colored glass filters are used which transmit a narrow range of wave lengths. In order to
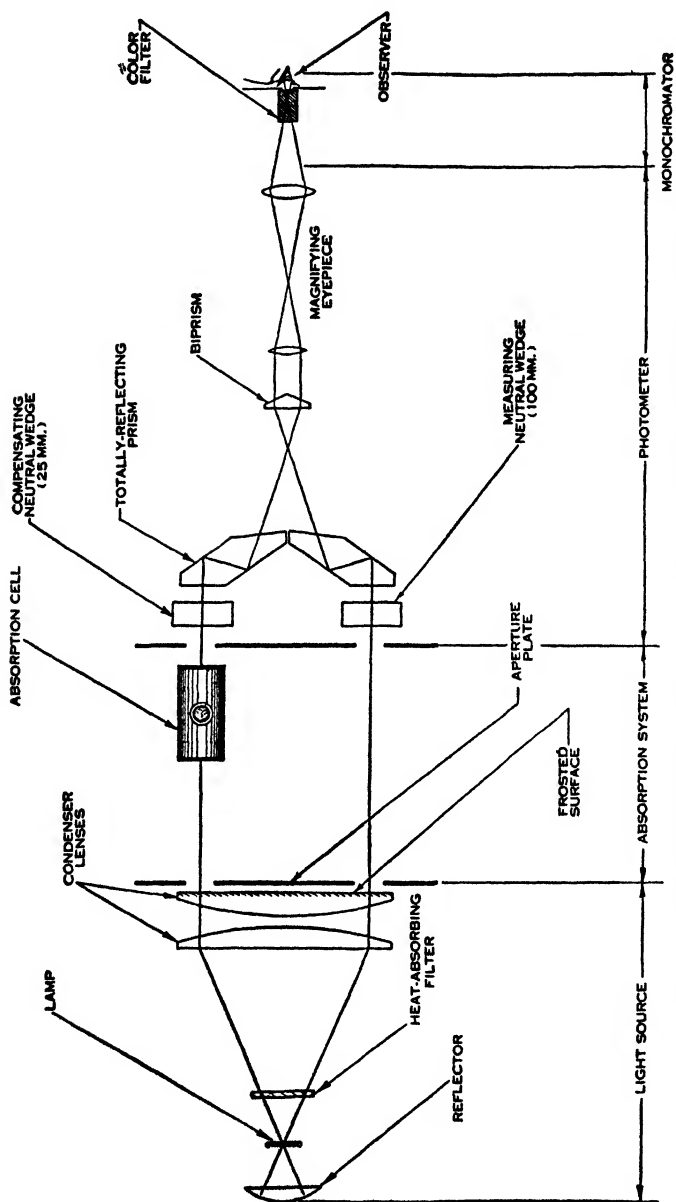
FIG. 114.—Neutral-wedge photometer.   (*Courtesy of American Instrument Company.*)

decrease the transmission of the sample and thereby increase the sensitivity, the color transmitted by the filter should be that most strongly absorbed by the sample.   Thus if the transmission curve of the sample is similar to that shown in Fig. 115, a filter should be chosen that transmits only in the spectral region marked by the dotted lines (*a*), due allowance being made for the spectral sensitivity of the eye.   Since the theories of spectrophotometry have been discussed elsewhere (Sec. 52), it is only necessary to point out here that the filter should transmit as narrow a band as is feasible and that this band must be centered in effect exactly at the lowest point in the transmission curve of the sample.   It is advisable to investigate the latter before
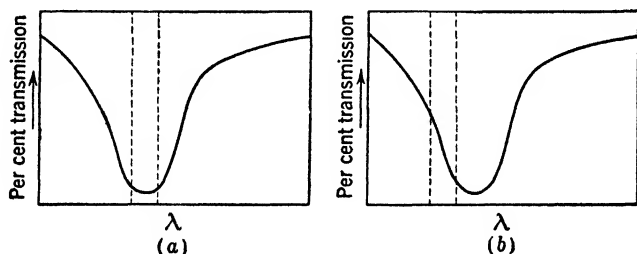
FIG. 115.

an analysis is attempted, because if the filter does not meet these specifications, the situation shown in Fig. 115*b* may result. Here the observed transmission will be several times larger, with a resulting decrease in sensitivity and, moreover, the two halves of the split field will not appear of the same hue which makes matching difficult.   Clifford and Brice[12] give details concerning the construction of "monochromatic" filters, although sets of filters may be purchased from various manufacturers.   Such filters may be used advantageously in conjunction with a Duboscq instrument, as mentioned in Sec. 72.   Truly monochromatic light of high intensity is easily obtained from a mercury-, cadmium-, or sodium-vapor arc equipped with suitable filters, and such a source should be used whenever the absorption minimum of the sample coincides with a bright spectral line.

An inexpensive neutral-wedge instrument known as a scopometer is available.[14]   In this device (Fig. 116), a neutral wedge adds to the absorption of the sample until the total transmission

is equivalent to the brightness of a portion of the field which is kept at a uniform low level.

It is possible to determine two or more colored constituents simultaneously provided that their transmission minima are far enough apart. The calculations outlined in Sec. 62 apply also to filter photometry. In this connection, and likewise in connection with the choice of filters, it is obvious that a wedge spectroscope would be of great help in the selection and development of any colorimetric procedure. Mellon[16] gives an account of the role of spectrophotometry in colorimetry.

The most accurate, and at the same time most elaborate, of colorimetric instruments are those which employ a polarizing device as a means of darkening one-half of the field.[15,36] These polarization photometers are similar to the Hilger-Nutting or Koenig-Martens photometers described in Sec. 47.

The Pulfrich photometer[17] is optically analogous to the Spekker photometer (Sec. 58) in that brightness is controlled by a variable diaphragm which is graduated in suitable units. The only available instruments of this type are very expensive, but they are widely used be-

Fig. 116.— Exton scopometer. (*Courtesy of Fisher Scientific Company, Bausch & Lomb Optical Company.*)

cause of their reputed accuracy. Each instrument is equipped with a rotating filter holder which permits rapid selection of the desired filter and also a rough estimation of the transmission curve of a sample.

The great advantage of a filter photometer over a Duboscq or two-solution instrument is that no reference solution is required. It is possible to calibrate the scale of a neutral wedge, polarization prism, or variable diaphragm by original measurements on a series of prepared standards. The scale reading is plotted vs. concentration to give a working curve, and all subsequent measurements on samples of unknown concentration are referred directly to this curve. A typical curve for the neutral-wedge photometer is shown in Fig. 117.

77. Photoelectric colorimeters[88] have now been developed to a point where they seem destined to replace visual instruments almost entirely. They present the advantages of virtually eliminating visual and personal errors and are relatively unaffected by slight differences in hue, *i.e.*, it is possible to match the brightness of, say, a blue and a green solution reproducibly. Furthermore, a well-designed photoelectric photometer is capable of as much as ten times the accuracy of the best visual instruments. The cost of the two types is not significantly different. Note in the following that photoelectric instruments may be designed either as one-solution or two-solution colorimeters. Owing to the great number of commercially available instruments, it is considered advisable to give only the fundamentals of each type of photoelectric photometer, of which there are only three.
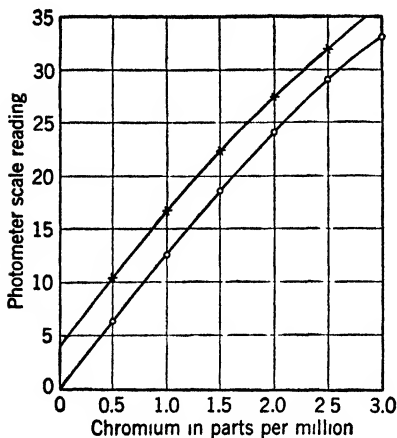
FIG. 117. Typical working curve (chromium analysis with neutral-wedge photometer).
Filter: No. 51. Peak at 515 mμ
Reagent: diphenyl carbazide 20 mg. in 1.0 ml. glacial acetic acid plus 9.0 ml. ethyl alcohol
Proportions: 0.2 ml. reagent per 10.00 ml. chromate solution. Allow to stand 30 minutes
Cell length: 1 in. (1.001 in.)
x Without reagent blank. No comparison cell.
° With reagent blank in 1-in. cell.

78. Direct-reading photoelectric photometers are simple in design and operation. The working principle is illustrated by the Sheard and Sanford instrument,[18] shown in Figs. 118 and 119, and it should be noted at once that an absolutely constant source of illumination is required. (Müller[19] states that the current I from the photovoltaic cell varies with the voltage V of the light source in accordance with the equation $I = kV^n$ where n is a constant approximately equal to 4.) The constant illumination from source S traverses an iris diaphragm and condenser before entering the solvent-containing cell C_1. The parallel rays pass through the latter and fall on the surface of the photovoltaic cell P whose output is read directly from the galvanometer G. The filter F must be used in nearly all cases.

In practice, it is usual to adjust the iris diaphragm until the transmission of the solvent causes a deflection of 100 on the galvanometer scale. The sliding carriage is then moved until
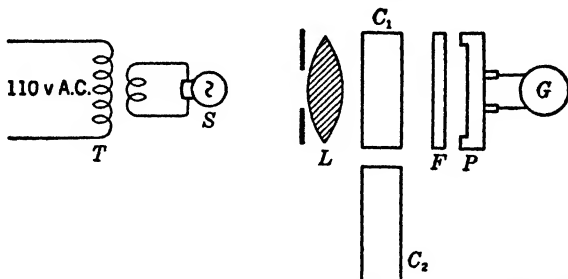
Fig. 118.—Direct-reading photoelectric photometer.   (*After Cenco Photelometer.*)

T = constant-voltage transformer
S = lamp
I = iris diaphragm
L = condenser
C_1C_2 = cells mounted in sliding carriage
F = filter
P = barrier-layer photoelectric cell
G = galvanometer
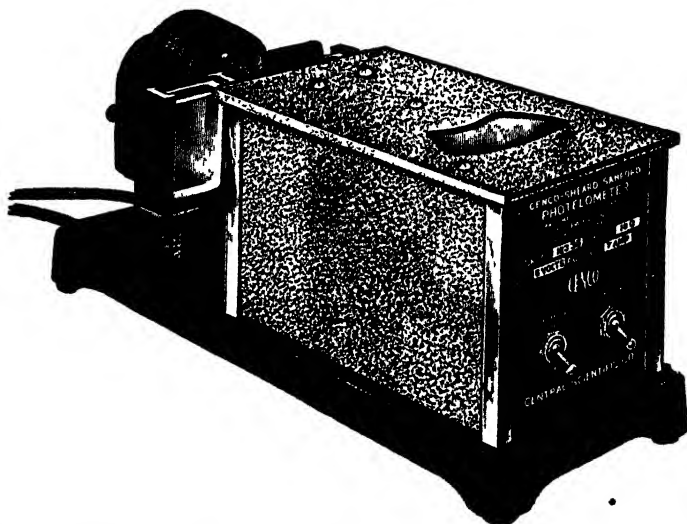
Fig. 119.—Cenco photelometer.   (*Courtesy of Central Scientific Company.*)

the solution cell intercepts the beam, when the galvanometer reads percentage transmission directly. It is customary to plot the logarithms of the transmissions of a series of prepared samples

vs. the concentration, in which case the working curve is usually found to be a nearly straight line.

An alternative and more sensitive setup employs a photoemission cell whose output is amplified thermionically. The rudimentary circuit is shown in Fig. 120, but more complex circuits are usually used.[19,20,21,22] Zinzadze,[23] Mellon,[24] and Strafford[25] give references to several instruments of this and other types.

In view of the fact that

Fig. 120.--Direct-reading phototube circuit (simplified).
P = phototube
T = amplifying tube
G = milliammeter

photoelectric elements are somewhat sensitive to the infrared region, it is usually necessary to use an infrared absorbing filter
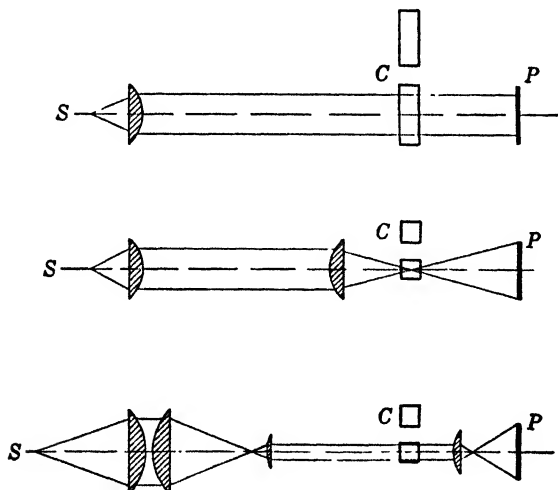
Fig. 121.—Optical systems used in photoelectric photometers. (*After Withrow et al.*)

S = source
C = cells
P = photosensitive element

somewhere in the optical system. · A liquid filter consisting of dilute aqueous copper sulfate is most effective, but filters of the Aklo type, made by Corning, may be used. It may be pointed

out that infrared photometry of "colorless" solutions is a well-nigh unexplored field which offers great promise.

The increased sensitivity of the photoemission tube results from the fact that its originally small output may be amplified, whereas this is not feasible in the case of the photovoltaic cell. Withrow *et al.*[26] list three optical systems that may be used in photoelectric photometers. These are shown in Fig. 121. It must be emphasized that an image should never be focused on the photosensitive element because the latter varies in sensitivity over its surface, and because, in the case of the photoemission tube, the surface may be injured by too intense illumination.

A very satisfactory direct-reading photometer originally described by Evelyn[27,28] is now available commercially. The diagram shown in Fig. 122 illustrates the principle. In this instrument, the galvanometer scale is adjusted to read 100 by controlling the lamp voltage by means of a series of resistances. The lamp is very small and is run at less than its rated voltage. Use of a test-tube absorption cell is convenient in that the cell itself may be used for carrying out the reaction, but cylindrical cells are liable to cause error because of their lens action. As stated, this latter difficulty arises principally from the varying sensitivity of different areas of the photocell surface but may be reduced by using specially selected test tubes and mounting them in a holder that permits no movement. Evelyn recommends that several dozen tubes be filled with a colored liquid and those which give readings more than 0.5 per cent from the mode be rejected. A modified apparatus for 0.1 to 2 cc. of solution is also described.[28]

Fig. 122.—The Evelyn photometer.

S = 6.2 volt flashlight bulb (Mazda #31)
A = 1 × $\frac{7}{16}$″ rectangular aperture
T = large test tube
F = filter
G = galvanometer (1000 Ω .025 microamp/mm.)
H = mercury-platinum low-resistance switch
P = barrier-layer cell

79. Potentiometer-type photoelectric photometers employ an electrical method of balancing the output of two photosensitive

devices. Summerson[29] points out several advantages for this type of circuit. The simple circuit shown in Fig. 123 operates as follows: Light from bulb L, which need not be of constant intensity, passes through two identical optical systems to photo-voltaic cells P_1 and P_2. The output of the two cells is balanced by the low-resistance potentiometer R, and then the absorption cells C_1 and C_2 are filled with solvent and solution or standard and sample, respectively. If the darker liquid is placed in C_1, the output of P_1 is diminished and the galvanometer G will show a deflection. The two circuits are then rebalanced by manipulating the potentiometer until the galvanometer again reads zero, when the potentiometer reading will be proportional to the ratio of the transmissions of C_1 and C_2. By choosing suitable resistances and using a graduated slide-wire, the scale of the latter
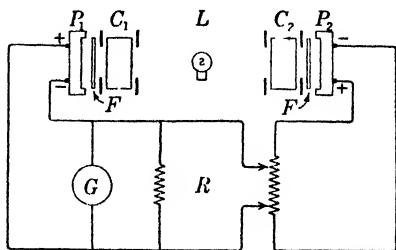
FIG. 123.—Potentiometer circuit.
(*After American Instrument Company*)

(a)   (b)
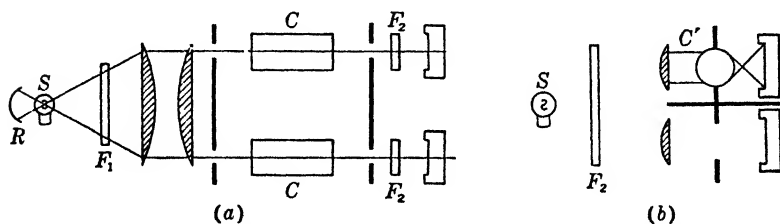
FIG. 124.—Other optical systems used in photoelectric photometers.

S = source
R = reflector
F_1 = heat-absorbing filter
F_2 = colored filter
CC = absorption cells
C' = test tube

may be made to read this transmission ratio directly. When C_2 contains pure solvent, then the ratio becomes the percentage transmission of the solution in C_1. The optical system of such an instrument may be that shown in Fig. 124a[30] or 124b[29] or it may include a light-dividing system of the type described in Secs. 47 and 58.

Withrow *et al.*[26] have described a very precise instrument of this type whose essential features are shown in Fig. 125.   An accuracy of 0.5 per cent is claimed for this device which is available in a
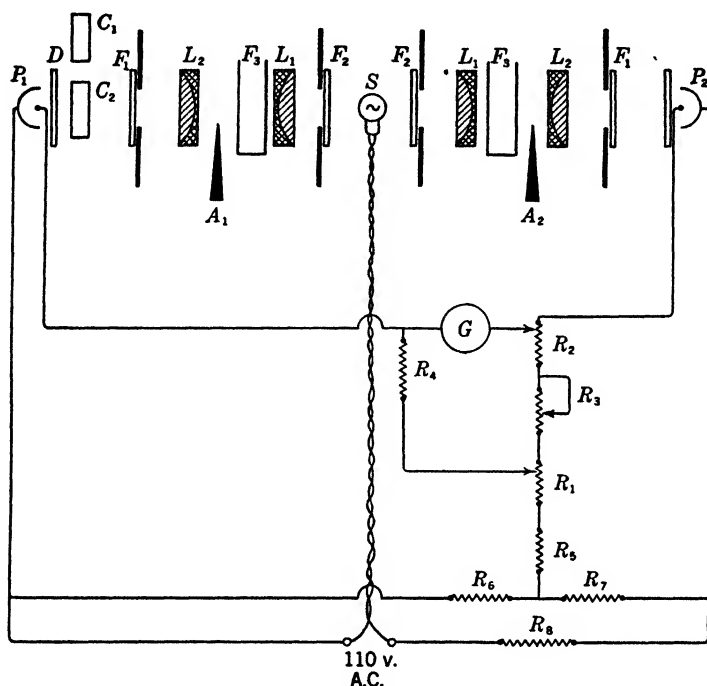
FIG. 125.—Precision photometer.   (*After Withrow et al.*)

S = 100-watt projection bulb
F_2 = heat-absorbing filter
L_1L_2 = condensing lenses
F_3 = liquid filter
F_1 = narrow band-pass filter
C_1C_2 = absorption cells
D = diffusing glass
P_1P_2 = cesium oxide phototubes
A_1A_2 = adjustors for balancing illumination
G = galvanometer
$R_1R_2R_3$ = dial decade resistors, 10,000-1,000-100 ohms
R_4 = fixed resistor, 10,000 ohms
$R_5R_6R_7$ = fixed resistors, 10,000 ohms
R_8 = fixed resistor, 1,000 ohms

modified form as the KWSZ photometer (Wilkens-Anderson Company).

The well-known Moll photometer uses the same principle as the photovoltaic device mentioned above, but the sensitive elements are thermopiles.   Willard[31] describes recent improve-

ments on the original design.   This type of instrument is said
to be very accurate.

Some instruments have been described in which the trans-
mission ratio is read directly from a galvanometer which indi-
cates the state of unbalance of two
photocell circuits (see Fig. 126).
Although such a circuit permits direct
readings on a galvanometer scale, the
balancing operation being thereby
eliminated, there is some question as
to its theoretical justification.   In
such a circuit, external current is
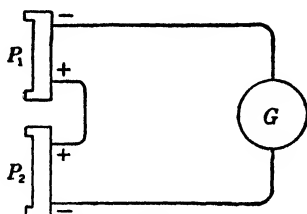
Fig. 126.—Unbalanced dual
circuit.
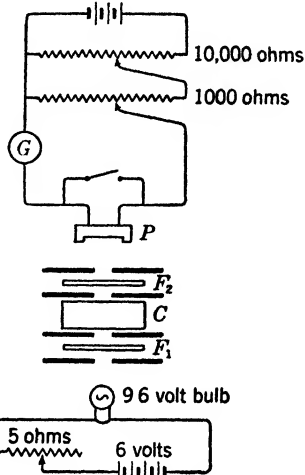
Fig. 127.

impressed across one or the other of the photocells whenever a
reading is made.   The response of the photocell may be altered
because of this.

Sullivan and Norris[32] describe a single-cell photometer which
nevertheless employs a balanced circuit.   Their instrument is
shown schematically in Fig. 127.   When the galvanometer
reads zero, the reading of the potentiometer is a measure of the
transmission.

A very ingenious means of balancing is employed in the
Lumetron colorimeter (Photovolt Corporation) shown in Fig. 128.
The calibrated slide-wire R is set on 100, and the balance cell is
adjusted until the galvanometer G reads zero when cell C con-
tains solvent.   The solvent is then replaced by the sample, and
the slide-wire R is turned until the galvanometer again reads
zero.   The slide-wire scale then gives the percentage transmis-
sion.   When very low transmissions are to be measured, the
neutral filter F_2 is used for the optical balancing of the circuit.
This procedure is said to be capable of multiplying the reading

nearly one hundred times, so that an actual transmission of 1 per cent will read 100 per cent on the slide-wire scale.
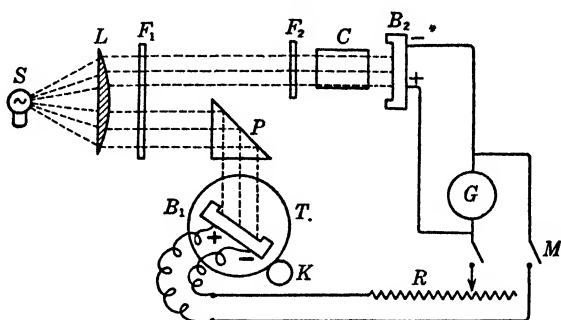
Fig. 128.—The Lumetron colorimeter (simplified).

S = lamp
L = condenser
F_1 = colored filter
F_2 = neutral-tint filter
P = reflecting prism
B_1 = compensating photocell in revolving mount
B_2 = measuring photocell
K = knob for turning mount
T = turntable mount with graduated scale
G = galvanometer for null reading
R = calibrated slide-wire
M = switch to convert instrument to direct-reading type

80. Optically compensated photoelectric photometers achieve a null reading by means of an optical arrangement.   The Hilger
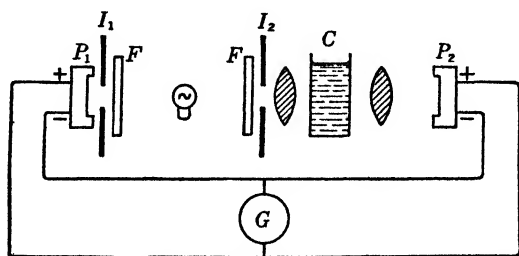
Fig. 129.—The Hilger Spekker absorptiometer (simplified).

P_1P_2 = barrier-layer cells
I_1 = ungraduated iris diaphragm for preliminary adjustment
I_2 = graduated iris diaphragm from which transmission readings are made
FF = filters
C = cell containing sample

Spekker absorptiometer, whose principle is illustrated in the simplified drawing (Fig. 129), operates as follows.   The circuit is balanced without the cell C in place by altering the aperture

of iris diaphragm I_1 when the calibrated aperture I_2 is set at zero. The cell C, containing the colored sample, is replaced and the calibrated aperture I_2 is opened until the galvanometer G indicates that the two circuits are balanced. The density $\log (1/T)$ is read directly from the scale of the calibrated aperture. Matched filters may be used when desired. A similar instrument (photoelectric scopometer) made by Bausch and Lomb employs phototubes instead of photovoltaic cells.

Many modifications of this and the other two types of photometers have been described in the literature, but these all use circuits and optical systems entirely analogous to those discussed in the last three sections. Several excellent reviews of photoelectric instruments are available,[20,21,23,21,33,34,35,36] and more than 40 descriptions of individual instruments have appeared in the literature during the past 10 years.

81. Errors of visual and photoelectric colorimetry are largely eliminated by scrupulous care of the instruments and by careful preparation of working curves whenever possible. In addition to Beer's law deviations, which have already been discussed, the following sources of error contribute to the inaccuracy of colorimetric measurements in general:

1. Mechanical errors and scale errors.
2. Unsymmetrical illumination, dust, etc.
3. Internal reflections in cells, stray light.
4. Contamination of solutions, excess reagent, etc.
5. Weighing and dilution errors.
6. Instability of color.
7. Temperature effects.
8. Personal errors.

The magnitude of these errors is dependent to a large extent on the type of instrument used. Many of them may be eliminated by means of the working curve, but the analyst must always bear in mind the possibility of their presence.

Mechanical errors and scale errors are easily checked by means of standards and by careful inspection of the instrument. Errors in photocell circuit,[22] design, galvanometer, and potentiometer come under this classification.

Unsymmetrical illumination may result from a variety of factors. In the case of the Duboscq and related instruments, care should be taken to see that the halves of the field match

when the cells are empty and when full of colorless solvent. In photoelectric instruments of the direct-reading type, the same precaution should be taken, *i.e.*, the same reading should be obtained for each cell. Cells and optical parts must of course be kept scrupulously clean.

Internal reflection and related effects are most pronounced in the Duboscq colorimeter when the height of the two columns of liquid differs by a large amount. This is true even for absolutely clear solutions. Stray light is a common and frequently unsuspected source of error, especially in photoelectric instruments. It may be reduced by the use of an optically black finish for all opaque parts and by inserting diaphragms or baffles in the optical path. One of the common sources of stray light is reflection of extraneous lateral rays by invisible suspended particles in the solutions. A lighttight cover over the instrument reduces this error but seldom eliminates it altogether. Note the number of diaphragms in the precision instrument shown in Fig. 125.

Solutions may be contaminated by foreign colorless materials which affect the color of the principal solute, by foreign materials which are themselves colored, or by suspended particles. Due precautions must be taken to guard against such effects, especially the first, which is seldom obvious. Little need be said concerning errors of weighing and dilution except to observe that both calibrated weights and corrected volumetric ware should be used.

The hue and brightness of a solution may be profoundly affected not only by foreign materials and solvent, but also by adsorption on the walls of the container, by temperature changes, and by the color of the illumination. The latter has a very pronounced effect, and the same source should always be used. The special illuminator (Fig. 111) and the chalet lamp (Fig. 154) are equipped with carefully corrected filters which should not be changed. Some materials, *e.g.*, dithizone or bromocresol purple, appear to be of different hue in different thicknesses. Such dichroic solutions must be examined at one fixed thickness.

Temperature changes affect colorimetric observations in divers ways, *e.g.*, through expansion of mechanical, optical, and electrical parts and through heating of the photosensitive element, if one is employed. The illuminator should be left on for several minutes before using a photoelectric or one-solution photometer, so that the lamp may reach a steady state and the mechanical,

electrical, and optical parts may expand to their usual dimensions. Whenever a photoemission tube is used, it should be protected from the effects of infrared radiation by a suitable filter.

One should never rely on the permanence of a color unless it has been demonstrated experimentally under the conditions employed. Neither should it be assumed that a sample and a standard will fade at the same rate. Transient colors are best compared with standards of almost identical composition whose rate of fading has been shown to be equal. If a one-solution comparison method is employed, as in the case of the neutral-wedge or single-cell photometer, then it is necessary to make a series of readings at known intervals after preparation of the solution and plot transmission vs. time. The original transmission is then found by extrapolation.

Under personal errors, one may list not only the unpredictable errors of both experienced and inexperienced observers but also the predictable physiological errors of vision. One person might obtain 10 consecutive readings by means of a Duboscq colorimeter, which do not differ by more than 1 per cent, whereas another will obtain differences of 10 per cent. If the color of the solution is changed, the foregoing results may be just reversed. The analyst should experimentally determine his own ability to match brightnesses of various hues so that he can estimate his visual error. Color blindness does not in general dull the judgment of brightness, and in some cases it results in improved sensitivity.

The general procedure that seems to give best results in the majority of cases involves the following points:

1. Three- to five-second observations, followed by a rest period of several seconds.

2. Use of only one eye, the other being kept closed during an observation; both eyes should be closed during the rest period.

3. Alternating approaches to the match point first from one side and then the other.

4. If glasses are worn habitually, they should not be removed for the observation.

5. To avoid fatigue, it is recommended that the field be no brighter than necessary and that the room be partly darkened.

82. Applications of Chemical Colorimetry.—Colorimetric determinations are, in general, applicable to chemical analyses when

the sought-for constituent is colored itself, as, for example, potassium permanganate or when it combines with a second component to form a soluble colored substance, or when it affects the equilibrium existing between two or more forms of a colored substance, *e.g.*, an indicator.

By far the greatest number of routine analytical procedures fall under the second heading. Nearly a thousand colorimetric methods of quantitative analysis have been worked out and used successfully for the determination of cations, anions, organic materials, and even gases. Many of the procedures are described in detail in the two standard works of Yoe[4] and Snell and Snell,[5] and in analytical publications.[37,38] Hoffman[92] gives clinical applications of the filter photelometer, and Freund[93] lists a number of clinical and analytical procedures. Mellon[24] in a recent critical survey of the field of colorimetry gives a lengthy bibliography and emphasizes the scope of the method by noting that Snell and Snell list 700 analytical procedures for the determination of 400 radicals, compounds, and elements.

In many cases, the color produced by the reagent may actually be caused by the extremely fine colloidal particles, as for instance, in the formation of Prussian blue, or alizarin lakes of various metals. Colors due to colloidal dispersions usually obey Beer's law within limits, provided that the "solutions" appear to be absolutely clear. Since the particle size has a considerable influence on the transmission of such dispersions, it is advisable to adopt a standard procedure for mixing, etc., and to employ a protective colloid such as starch, starch glycerite, gum arabic, gelatin,[4,39] organic detergents, or wetting agents.

The colorimetric method is most generally used for the analysis of solutions whose concentration is so low that ordinary gravimetric or volumetric methods involve large errors, although the method is also applicable when the concentration is well within the range of conventional methods. Murray and Ashley[40] report the determination of nickel in concentrations ranging up to 20 per cent with an accuracy of 0.2 per cent.

The lower limit of sensitivity is determined by chemical considerations, the coloring power of the solute, and the ability of the analyst to overcome the difficulties inherent to work with small quantities. This latter factor is more significant than is generally conceded and perhaps deserves a word of explanation.

The ability of the analyst involves personal manipulative skill, use of an instrument of sufficiently high precision, and the elimination of the many sources of error always encountered in work with minute quantities.   This latter point may be stressed by mentioning that the sensitivity of a method for determining lead is to some extent limited by the fact that traces of lead may be adsorbed by Pyrex bottles or cells that have been previously treated to remove whatever lead was originally present in the glass.

The upper limit of concentration is largely determined by the accuracy required.   A 2 or 3 per cent error, which is negligible when dealing with quantities of the order of parts per million, becomes serious when concentrations are in the vicinity of parts per hundred.   The colorimetric method has nevertheless been used for rapid routine analyses of solute concentrations up to 20 parts per hundred.

Attention should be directed to the increasing use of organic reagents for the determination of inorganic ions.   Recent researches in this field have been particularly fruitful, and many very sensitive reagents are now available (see Feigl,[41] Yoe and Sarver,[42] Mellan,[43] and Prodinger[85]).

Mention has already been made of the possibilities of infrared photometry which have not yet been explored.   Ultraviolet photometry has, however, been developed to the point of practical application in the determination of vitamin A.[44,45]   The photoelectric instruments employed are structurally similar to those discussed in the preceding sections but differ in that monochromatic ultraviolet sources are used.   The sodium line at 330 mμ or the copper line at 327 mμ, which are isolated by suitable filters, seem to be most suitable, since vitamin A exhibits a strong absorption in the vicinity of 328 mμ.   Demarest's paper[87] is particularly informative and contains a discussion of the statistical uncertainty of photometric measurements in general.

The principal requirements, disadvantages, and advantages are summarized for the sake of convenience in Table 9.

Determination of pH.—The colorimetric method of determining pH is used to a considerable extent because of its simplicity and rapidity.   The Walpole technique is employed for rapid, approximate determinations, either buffer solutions plus indicator or glass plates being used as standards.   The choice of

TABLE 9.—TABULAR SUMMARY OF CHEMICAL COLORIMETRY

1. *Requirements of Colorimetric Procedures:*
    a. The color produced by the reagent should be specific; or interfering constituents should be easily eliminated.
    b. The color produced by the reagent should not be affected by varying amounts of other constituents, and it should not be unduly sensitive to changes in pH.
    c. The hue of the solution should not be greatly affected by concentration, and Beer's law should be obeyed within reasonable limits.
    d. The color should develop rapidly and be moderately permanent.
2. *Advantages of Colorimetric Procedures:*
    a. Ease and rapidity are the primary advantages.
    b. The method is particularly useful in the low-concentration range where ordinary chemical methods fail, and in some cases it is even superior to the spectrographic method in sensitivity and accuracy.
    c. The method is almost universally applicable, and in some cases as many as three substances may be determined simultaneously by choice of proper filters.
3. *Disadvantages of Colorimetric Procedures:*
    a. Highly accurate procedures are as time consuming as ordinary gravimetric analyses (if the latter can be used).
    b. Large personal errors are possible.
    c. Many common reagents are not specific. Failure to recognize this fact may lead to a systematic and undetected error.
    d. The method is practically limited to determination of small concentrations, since taking aliquot parts multiplies the error (however see Murray and Ashley[40]).

indicator is determined by the pH range to be covered and by the requirement that the indicator show a transition color between the acid and alkali colors. A wide-range indicator is commonly used to determine the pH to ± 0.5 over the range pH 3 to pH 11. Phenol red (pH 6.8 to 8.4) and bromothymol blue (pH 6.0 to 7.6), etc., are usually employed for the final measurement to ±0.1 pH, although a large variety of indicators are available for narrow ranges.

For more accurate work, it is necessary to dispense with troublesome and unstable buffer mixtures and to employ a more precise optical method of comparison. The Duboscq or wedge-type of bicolorimeter is widely used for pH measurement to better than ±.05. The principle of the bicolorimeter is shown in Fig. 130, where P, P' represent the hollow plungers and C, C' represent the cups of a modified Duboscq colorimeter. The auxiliary cup B alone is movable and is attached to a scale graduated from 1 to 100 whose length corresponds to the fixed

distance from the bottom of the plungers PP' to the upper surface of the bottom of cells CC'. To obtain the pH of a solution, a two-color indicator of suitable range is selected and a slightly acid solution of the indicator is placed in cell C. An alkaline solution containing the same amount of indicator is then pipetted into cell B, and the solution of unknown pH plus the same amount of indicator is placed in cell C'. By moving B up or down, the color observed through P is made to change progressively from that of the acid form of the indicator to that of the alkaline form, and at some position of B it will match the color of the solution in

Fig. 130.

C'. The reading of scale S then gives the ratio B/A of the basic form to the acid form of the indicator. The pH of the unknown solution may be computed from the equation
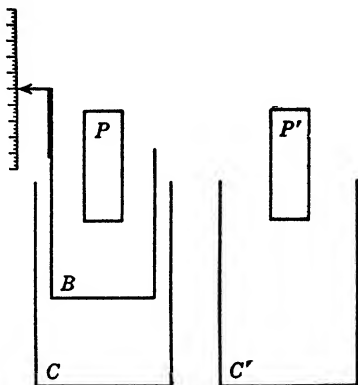
$$\mathrm{pH} = \log\left(\frac{B}{A}\right) + pK$$

where pK is a constant characteristic of the indicator. This constant varies slightly, however, with the ionic strength of any electrolyte that may be present, and it is therefore necessary to apply a small correction.

83. Experimental.—In lieu of presenting detailed directions here, the student is referred to one of the general references cited on page 156. The following analyses should be carried out:

1. Determination of copper by the blue ammonia complex, according to Snell and Snell.[5] Use the Walpole comparator and a series of prepared standards whose concentration ranges from 0.01 to 0.1 mg./cc.

2. Determination of phosphorus in steel by the use of the phosphovanadio-molybdate reagent and either Nessler tubes or Hehner tubes. Use of a split-field comparator is recommended. An alternative determination is that of nitrogen by the Nessler method, although this requires slightly more time.

3. Determination of pH with a Hellige comparator. Use the wide-range indicator to determine what narrow-range indicator is most suitable.

4. Determination of chromium by diphenylcarbazide.[5] Use a Duboscq instrument, a neutral-wedge or other type of single-cell photometer, and a photoelectric photometer. A filter transmitting a narrow band centered at 520 mμ should be used in the latter cases. Compare the three instruments in regard to accuracy.

THE TURBIDIMETER

84. The colorimeter and the turbidimeter resemble one another in that each is a device for measuring or comparing the relative transmission of liquids. The turbidimeter, however, is a colorimeter intended primarily for use in determining the transmission of cloudy or turbid suspensions, in which case the turbidity is assumed to be a function of concentration. The degree of turbidity T is thus analogous to the absorption A of colored solutions, although the mechanism of the "absorption" of light by colored molecules is quite different from that by suspended opaque particles.

85. The relation of turbidity to concentration has been the subject of considerable theoretical study which will be considered in Sec. 92, but the practical analyst need bear in mind only the following facts. (1) It is necessary to determine experimentally whether or not a given reaction may be made to give a suspension of suitable properties. (2) The optimum procedure for preparing the suspension having been determined, it is necessary to adhere to it rigidly, to the last minor detail. (3) It is then necessary to prepare a working curve or plot of concentration vs. scale reading, since the relation of concentration to turbidity is quite complex and almost never precisely linear.

86. Turbidimeters may be simply colorimeters of any of the several types discussed in the foregoing pages. Nessler and Hehner tubes, the Duboscq colorimeter, and other colorimetric instruments may be used for turbidimetric measurements, provided that the sides of the absorption cells are well shielded from extraneous light. This is generally accomplished by means of an optically black jacket or sleeve, which is placed in contact with the sides of the cell. If a filter photometer is used, it is

sometimes possible to evaluate the turbidity of *colored* solutions by choice of suitable filters. Nees[46] describes a method that is applicable in some cases. Measurements of absorption are made with two different colored filters, one of which is complementary to the color of the solution.

Let a = total percentage absorption for light of color A.

b = total percentage absorption for light of color B.

c = percentage absorption for light of color A due to colored solute alone.

c' = percentage absorption for light of color B due to colored solute alone.

T = percentage absorption for light of color A due to suspension alone.

T' = percentage absorption for light of color B due to suspension alone.

Then

$$c + T = a \qquad \frac{c}{c/c'} + \frac{T}{T/T'} = b$$

The ratios c/c' and T/T' are determined independently, with synthetic solutions showing only color and only turbidity, respectively, and the equations solved for c and T.

A second group of instruments known as *extinction turbidimeters* are designed especially for turbidimetry. The Jackson candle turbidimeter shown in Fig. 131 is one of the older types, which is, however, still widely used for industrial testing. The turbid liquid is poured into the Hehner cylinder until the outline of the candle flame viewed from above just disappears. The height of the meniscus is then read and applied to a previously constructed working curve.

A more elaborate device working on the same principle is the Burgess-Parr turbidimeter[47] shown in Fig. 132. A small electric bulb D is maintained at a definite voltage by resistance E. The filament is viewed through a column of

Fig. 131.—The Jackson candle turbidimeter. (*Courtesy of Central Scientific Company.*)

turbid solution in a glass-bottomed cell C whose depth l is indicated. The depth of the column is increased by raising the empty

glass-bottomed plunger A. An attached millimeter scale is read when the outline of the lamp filament is just obscured. This instrument, which is principally employed in the estimation of
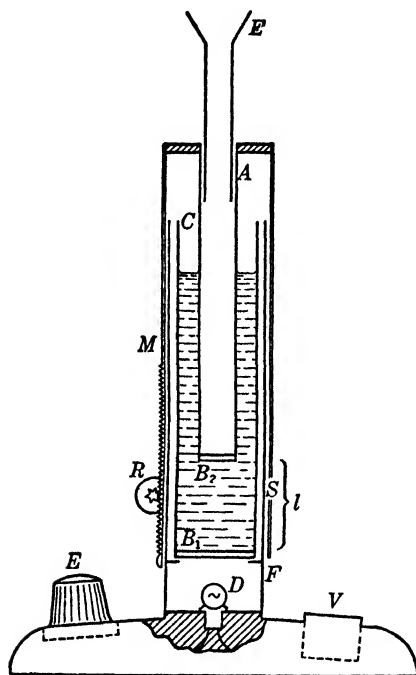
Fig. 132.—The Burgess-Parr turbidimeter.

E = rubber eyecup
A = glass-bottomed moveable tube
C = glass-bottomed cell containing turbid solution
B_1B_2 = glass windows
D = flashlight bulb
F = metal tube
M = outer metal jacket
R = rack and pinion for raising M and A
S = opening in M through which scale on F is read
l = depth of column of solution (read on scale)
V = voltmeter
E = variable resistance

sulfate as barium sulfate, is capable of considerable accuracy. Parr's figures indicate that the scale reading is accurate to about 3 per cent in the middle of its range. A photoelectric turbidimeter of this design is also on the market (Burgess-Parr).

The Betz-Hellige combination turbidimeter,[48] shown schematically in Fig. 133, presents a novel working principle. The instrument is in effect both a turbidimeter and a nephelometer. Light from an opal glass bulb B passes through a micrometer precision slit S, is reflected by mirror MR, and passes through the turbid suspension to form the inner portion of an annular split field. The outer portion of this field is illuminated by light scattered by the suspension which is illuminated laterally by reflection R. The slit S is adjusted until the two portions of the field appear of the same brightness, and the reading of the slit micrometer is taken as a measure of concentration.

Other turbidimeters are described by Baylis[49] and Olszewski.[50]

87. Applications of turbidimetry are somewhat limited by the requirements mentioned above, especially that imposed by the nature of the suspended particles. These suspensions must be very fine and neither fibrous nor flocculent. Of course, it is possible to ensure stabilization of many suspensions and also to control their particle size by adding suitable hydrophilic colloids such as gelatin, starch, gum arabic, or egg albumin, but such a procedure must first be worked out by lengthy experimental investigation. Some suspensions are effectively stabilized by the presence of certain ions. Traces of acid, alkali, etc., are very efficient stabilizers for various suspensions[4,52] as are organic wetting agents.

Fig. 133.—Betz-Hellige turbidimeter. (*Courtesy of Hellige Inc.*)
P = plunger to eliminate meniscus
T = cell containing suspension
M = annular mirror
MR = mirror
S = precision slit actuated by graduated knob
B = diffuse source
R = reflector

One of the principal uses of turbidimetry is the determination of sulfur or sulfate in foodstuffs[51] and water[47,48] by conversion to barium sulfate. This is accomplished by adding an excess of solid barium chloride to a dilute solution of the sulfate, containing sodium chloride and hydrochloric acid. Barium sulfate precipitates under these conditions in the form of an almost colloidal

suspension. The method gives good results down to concentrations of a few parts per million.

The turbidimeter is also used for the determination of particle size and particle-size distribution.[53] One of the several specialized uses of a photoelectric turbidimeter is the detection of the first appearance of turbidity in a precipitation-titration reaction where a precipitate indicates the end point. The precipitant is run from a burette directly into the turbidimeter cell until the instrument registers a perceptible deflection.[54] This method of indication is extremely sensitive and is used for a number of routine titrations.

88. Standards of turbidimetry are usually made from suspensions of fuller's earth or diatomaceous earth in distilled water. The fuller's earth is passed through a 200-mesh sieve, and a weighed portion is shaken with distilled water. A suspension of 1 p.p.m. has a turbidity of unity on the arbitrary scale used for water analysis.[55]

THE NEPHELOMETER AND FLUOROPHOTOMETER

89. These two instruments are so similar in principle and design that they will be considered together. Each depends on measurement of light scattered at right angles to an intense illuminating beam. In the case of the nephelometer, the light is produced by true scattering, *i.e.*, by reflection and diffraction of light by tiny dispersed particles, whereas in the fluorophotometer, the light is produced by fluorescence of dispersed molecules. The term nephelometer, incidentally, comes from the Greek *nephelos*, meaning a cloud.

90. Scope of the Nephelometric Method.—The nephelometric method is generally applicable to quantitative reactions where a fine, preferably colorless, insoluble precipitate is formed. Most precipitates may be obtained in the form of a fine homogeneous suspension, which is stable for 10 minutes or more, by altering the usual conditions of precipitation. Use of lyophilic protective colloids or ionic peptizing agents is necessary in some cases. Yoe and Kleinmann[56] list 160 ways of determining 62 substances by nephelometric methods.

The sensitivity of which the nephelometric method is capable is best attested by the fact that phosphorus is detected in con-

centrations as low as 1 in 333 million parts of water[57] and acetone in concentrations of 1 in 100 million.[58]

91. Nephelometric instruments, in general, resemble colorimeters, with the sole major difference that the cells containing the turbid media are illuminated at right angles to the direction of observation.   One of the most common instruments is a Duboscq colorimeter modified by plunger shields and a suitable illuminator, as shown in Fig. 134.   The turbid sample is placed in one cell and a standard of known turbidity or concentration in the other. The illuminated depth of the two columns of liquid is adjusted by
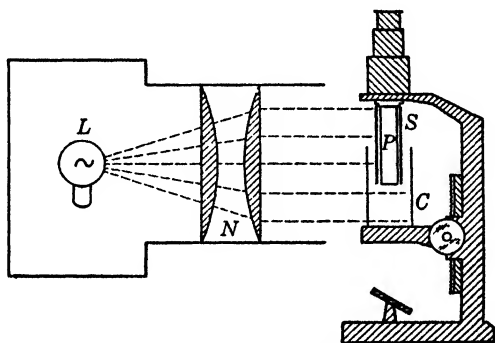
FIG. 134.—Illumination of nephelometer.
L = concentrated filament bulb or mercury arc
N = condenser
P = plunger
S = opaque sleeve accurately fitted over plunger
C = colorimeter cup

moving the cups until the two halves of the field match in brightness, and the millimeter scale reading of the instrument is noted and applied to a previously prepared working curve, from which the concentration of the unknown sample is obtained directly. The accuracy of such a measurement is considerably increased by use of the "tare" method of balancing described in Sec. 73. This latter procedure is particularly advisable for nephelometric analyses because of the large errors that may arise from unnoticed imperfections in the cells and plungers and because of the relatively large effect of slight differences in the intensity of the illumination.   The lamp and condensing system should be rigidly attached to the colorimeter base, or both units should be fastened to the table top.

Grant and Booth[59] describe a simple method of adapting the Duboscq instrument for use as a nephelometer by means of simple accessories, although the requisite parts are commonly available from manufacturers of Duboscq colorimeters. The opaque sleeves which cover the plungers are adjusted by filling both cups with water within a few millimeters of the top and
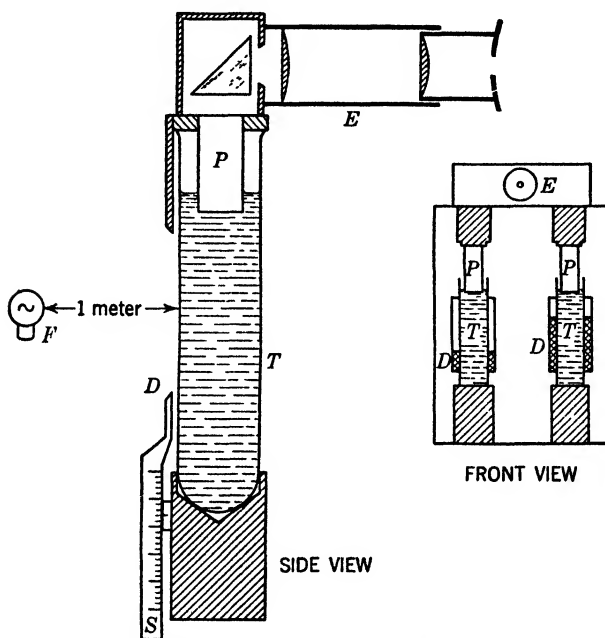
Fig. 135.—The Kleinmann nephelometer (simplified).

F = frosted 300-cp. bulb
D = movable part of rectangular aperture
S = scale
T = test-tube cell containing suspension
P = glass plunger to eliminate meniscus
E = eyepiece and light-dividing system

immersing the plungers. Both scales are set to zero, and the sleeves are moved up or down on the plungers until both halves of the field become perfectly black. The edges of the sleeves should then coincide with the ends of the plungers. It is sometimes feasible to use a heavy coat of black asphalt paint on the plungers, although this is subject to obvious disadvantages.

The Kober, Bloor, and other nephelometers of this general type are described by Yoe and Kleinmann in their standard work

on nephelometry.[56] The Kleinmann nephelometer, shown schematically in Fig. 135, operates on a similar principle but employs a calibrated aperture or window which controls the illuminated depth of the cell. A complete description of this instrument and a bibliography of Kleinmann's work is given in the above-mentioned text.
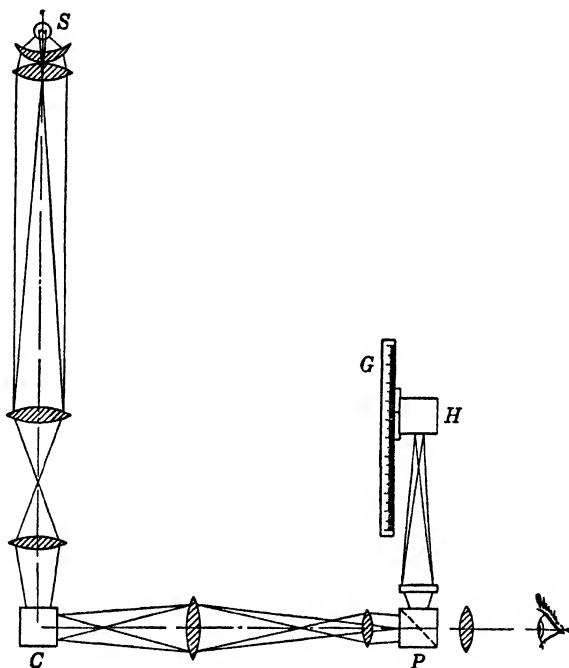
FIG. 136.—Tyndallmeter (nephelometer for very clear liquids). Light from source *S* is concentrated on the sample in cell *C*. Scattered light is brought to the photometer cube *P* where its brightness is compared visually with that of the luminous surface *H* which may be moved back and forth on scale *G*. (*After Cummins and Badollet.*)

Neutral-wedge nephelometers are described by Marshall and Banks[60] and Exton.[61] The Exton instrument is an adaptation of the scopometer for turbidity measurement (see also references 62 and 63).

Various photoelectric nephelometers, which are simply modifications of several of the photoelectric photometers described in Sec. 78, are described in the literature, although the Kober Duboscq type nephelometer seems to retain its place as the most popular precision instrument.

Ingersoll and Davis[64] have described an entirely novel device for nephelometry which operates on the extinction principle, and Cummins and Badollet[65] have designed a very elaborate Tyndallmeter for examination of very clear liquids (see Fig. 136). Control of the clarity of filtered liquids, sirups, etc., is quite important industrially. Zerban and others[66] have reported on the use of tyndallmetry in control of sugar sirups.

92. Errors in Nephelometry.—It is important to note that the usual instrumental and observational errors of nephelometry are often smaller than the errors that arise from the preparation of the precipitate. Thus it is possible to prepare two samples of turbid solution whose concentrations are identical but whose observed turbidities differ by 50 per cent. Accuracy and reproducibility are therefore more a function of the conditions of precipitation than of the precision of the instrument used.

Filtered white light may of course be employed, but the best results are obtained by using strictly monochromatic light from a mercury-vapor arc and filter. The exceedingly intense high-pressure capillary arc is an ideal source, since the green line at 546 mμ is not only very strong but is easily isolated.

Visual errors may be reduced further by taking all due precautions against extraneous light and glare. The operator should work in a darkened or semidarkened room and should accustom his eyes to the field of the nephelometer by making practice determinations at 1-minute intervals for 10 minutes or so.

Instrumental errors are largely eliminated by using the tare method of balancing referred to above. Due care must be taken to choose cups and plungers that are free from striations or flaws, and the instrument should be checked with a sample of freshly distilled water. The field should appear nearly black, irrespective of the positions of the cups or plungers. If desired, the equivalence of the two sides of the instrument may be checked by placing identical turbid solutions in each cup. Failure of the two halves of the field to match when the plungers rest on the bottoms of the cells may be due to unsymmetrical illumination or to other factors mentioned above.

Little can be said about the cause and prevention of errors due to the suspension, except that once a suitable method of preparation[67] has been found, it should be adhered to without any deviation whatsoever. The temperature, the quantity of reagent,

protective colloid, or foreign ion, the rate, and even the order of mixing should not be changed in the slightest once the optimum conditions have been decided upon.   Yoe and Kleinmann,[56] who give a complete discussion of this matter, list the following requirements of a nephelometric suspension:

1. Insolubility of the precipitate.
2. Absence of pronounced color and foreign particles.
3. Concentration of less than 100 mg./liter.
4. Apparent homogeneity of the suspension.
5. Stability for more than 10 minutes (with or without stabilizer).
6. Concentration of standard not greater than four times that of the sample.
7. If a reference suspension of different nature is used, it should be of nearly the same dispersive power as the sample.

Although no exact theoretical relationships between turbidity and concentration have been worked out, several approximate relationships are known.[68,89,91]   The work of Wells,[69] reviewed by Yoe and Kleinmann, is interesting to the practical analyst only in so far as it furnishes a rough idea of the effect of various factors on turbidity.   Wells's article, which is based on the original work of Tyndall[70] and Rayleigh,[71] includes the following approximate equation which relates the density or turbidity T to the concentration c of the turbid medium:

$$T = k \frac{cld^3}{d^4 + \alpha \lambda^4}$$

In this equation, k is a constant depending both on the medium and on the method of measurement, α is a constant for the method only, l is the thickness of the layer of medium, d is the average diameter of the suspended particles, and λ is the wave length of the illumination.   Although this equation holds only for dilute dispersions in thin layers, it illustrates the effect of several factors.   The great effect of wave length should be noted especially, as well as the implication that turbidity reaches a maximum when $d/\lambda = (3\alpha)^{1/4}$.   The equation also implies that Beer's proportion holds for dilute suspensions, since, when the turbidities of two suspensions of the same kind are equal,

$$k \frac{cld^3}{d^4 + \alpha \lambda^4} = k \frac{c_1 l_1 d^3}{d^4 + \alpha \lambda^4} \qquad \text{or} \qquad \frac{c}{c_1} = \frac{l_1}{l}$$

This simple proportion is actually not valid for the majority of nephelometric or turbidimetric determinations, even when monochromatic light is employed.

The Tyndall effect[70] is sometimes a cause of error. Tyndall observed that the light scattered by a bluish suspension of very fine particles was completely polarized in a plane at right angles to the axis of the lateral illuminating beam. The degree of polarization decreases rapidly, however, as the fine particles coalesce to form the larger particles of a typical turbid solution.

93. Deviations from Beer's law are easily expressed by the Kober formula given in Sec. 74, or by plotting a working curve. The Y reading referred to in Sec. 74 is plotted against the R value
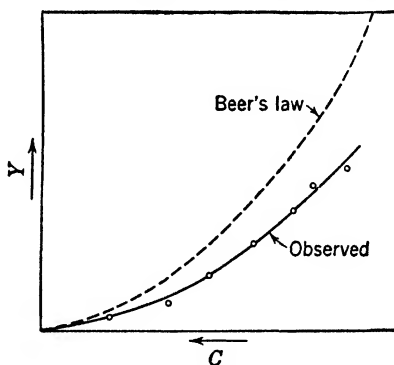
Fig. 137.

or the concentration to give a curve as shown in Fig. 137. The abscissas are reversed because, in contrast to the colorimetric method, the field of a nephelometer is brighter, the larger the concentration of the sample. The dotted curve is that predicted by the Beer's law proportion, and the fact that for a given value of Y the actual curve gives a higher concentration than the theoretical curve indicates that there are no appreciable losses due to solubility of the precipitate. This factor is also shown to be negligible by the constancy of Kober's constant K over a wide range of concentrations. For checking deviations from the dilution law, a solution of specially purified glycogen or starch is sometimes used as the reference substance, or a suspension of fuller's earth or silica. Reference standards are discussed by Yoe and Kleinmann,[56] who also suggest the use of opal glass and frosted tubes as standards.

94. Applications of Fluorophotometry.—A fluorophotometer is a nephelometer whose illumination is especially designed to excite measurable fluorescence of the clear sample.   Since the ability to fluoresce is not characteristic of all substances, the fluorophotometric methods of analysis may therefore be applied only to certain materials.   The number of substances to which the method has been applied successfully is increasing rapidly, however, and now includes more than a score of biological substances. By combining with a suitable organic complex, it is possible to determine unbelievably small amounts of inorganic ions.   Aluminum, for example, is determined in concentrations of the order of parts per hundred million.   One of the greatest applications of fluorophotometry is the rapid determination of riboflavin (vitamin B_2) and thiamin (vitamin B_1) in biological extracts where the concentration may be in the vicinity of 10 μg/liter.

White[73] gives a bibliography of some of the more important applications to inorganic analysis as well as an excellent discussion of the practice of fluorophotometry.   Hand,[74] who has designed a very successful instrument, also gives a brief bibliography. The work of Gotó[75] on fluorescence analysis is ably reviewed in *Chemical Abstracts*,[76] although no fluorophotometric applications are mentioned.   Danckwortt[77] and Haitinger[78] give a great deal of information on the use of fluorescence in analytical work.

95. Fluorophotometers are somewhat more accurate and easier to operate than nephelometers because of the relatively greater purity of fluorescence as opposed to diffuse opalescent reflection. It is also possible to eliminate stray light from the source by an ultraviolet absorbing filter which allows only the fluorescent radiation to pass.

Early fluorophotometers consisted of test tubes illuminated laterally by a source of ultraviolet.   Supplee *et al.*[79] used this method successfully for determining riboflavin.   A Duboscq type nephelometer was used by Josephy,[80] who employed fluorescein as a fluorescence standard.   A strong source of ultraviolet, from which visible light was removed by a filter, was used as the source.   White and Lowe[81] used a Pulfrich photometer in a similar manner.   Photoelectric fluorophotometers are now used almost exclusively because of their simplicity, accuracy, and objectivity.   One of the first of these, described by Cohen,[82] is shown diagrammatically in Fig. 138.   The simple instrument

of Hand[74] (Fig. 139) is easily constructed and gives excellent results.   A cube of fluorescent uranium glass is used to standard-
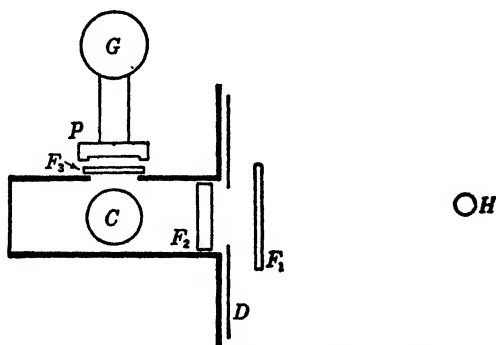
Fig. 138.—Fluorimeter.   (*After Cohen.*)

H = mercury arc
F_1 = filter to remove infrared
F_2 = filter transmitting only ultraviolet
F_3 = filter transmitting only visible light
C = test tube containing fluorescent sample
P = barrier-layer cell
G = galvanometer
D = diaphragm
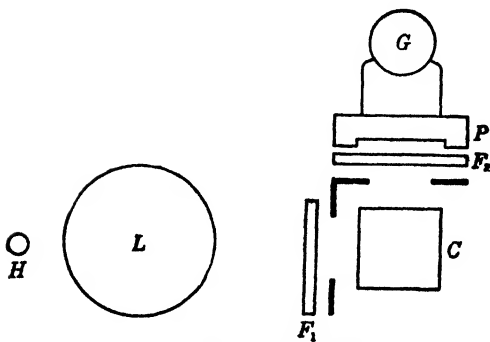
Fig. 139.—Fluorimeter.   (*After Hand.*)

H = mercury arc
L = water-filled flask acting as condenser
F_1 = Corning 585 filter isolating ultraviolet
F_2 = Corning 351 filter transmitting yellow only
C = lower portion of 30-ml. square bottle
P = barrier-layer cell
G = galvanometer

ize the readings.   An instrument of this type is commercially available (Fig. 140).   The instrument shown in Fig. 141 is somewhat more elaborate and is available commercially (Klett

Manufacturing Co.).   The balanced circuit eliminates errors due to fluctuations of the lamp intensity.
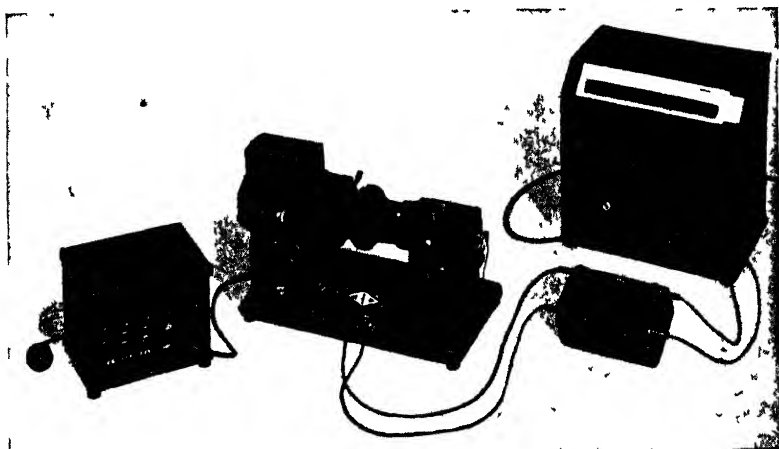
Fig. 140.—Fluorophotometer. May also be used as a filter photometer.
(Courtesy of Pfalz and Bauer, Inc.)
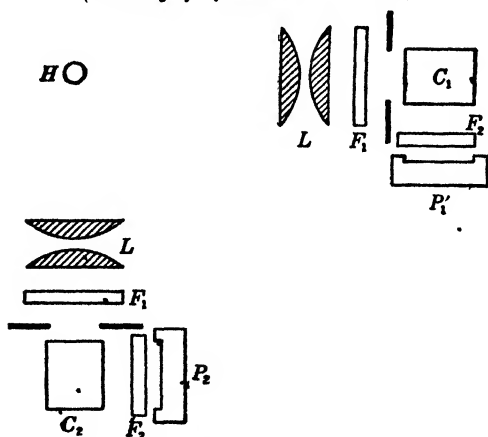
Fig. 141.—Fluorimeter.

H = mercury arc
LL = condenser
F_1 = filter to isolate ultraviolet
F_2 = filter to isolate fluorescent radiation
C_1 = cell for fluorescent standard (quinine sulfate solution)
C_2 = cell for sample
P_1P_2 = barrier-layer cells connected in a balanced potentiometer circuit

96. Calculations of fluorophotometry are based on the modified Beer's law expression

$$E = \log \left(\frac{F_o}{F_o - F} \right) = kcl$$

where E = extinction.

F_o = intensity of fluorescence of standard.

F = intensity of fluorescence of sample.

k = specific or molecular extinction for a given wave length of the exciting radiation.

c = concentration.

l = depth of column of liquid.

This equation resolves itself into the simple Beer's law proportion when a Duboscq type of fluorophotometer is used. Kavanagh[5] uses a similarly derived relation to express the results obtained with a constant-depth potentiometer-type instrument, *viz.*,

$$P = KI(1 - 10^{-kcl}) = KIf$$

where P = the potentiometer reading.

K = a constant depending on the instrument.

I = intensity of exciting radiation.

k = specific (or molecular) extinction for a given wave length of the exciting radiation.

c = concentration.

l = active diameter of the photocell.

f = intensity of fluorescence.

When a standard fluorescing solution of, say, 1 mg./liter of quinine sulfate is used as a reference, then for a given instrument and sample the variables in the preceding equation are P or f and c. These may be related graphically by plotting a working curve, or the constant factors in the foregoing equation may be evaluated experimentally and calculations made from the equation itself.

It is almost always necessary to correct for a slight fluorescence of the solvent, which is sometimes due to impurities and sometimes due to the solvent itself. The effect of turbidity or isolated reflecting particles is almost completely eliminated by the ultraviolet absorbing filter placed over the photocell, since all light from the source is thereby cut out.

It is sometimes possible to correct for the fluorescence of foreign materials by destroying the sought-for constituent chemically and noting the residual fluorescence. In almost

every measurement, there is danger that the fluorescent material will be subject to photochemical decomposition, which is usually indicated by a steady fall in successive readings.   In such cases, it is customary to plot these readings against time and extrapolate to zero time.   A more rapid but less accurate procedure is to take one reading at a specified time after placing the sample in the instrument.   The interval should be as short as possible but must give ample time for the performance of all necessary operations.

97. Experimental.   *The Turbidimeter.*—1. Examine the Burgess-Parr instrument, and note whether the cell windows are clean when dry.   If not, they may be cleaned with a saturated solution of ammonium acetate applied with a rag attached to a dowel, which is tipped with a short piece of stiff rubber tubing.

Weigh 0.6647 g. anhydrous sodium sulfate, and dissolve to make 1 liter.   This solution should contain 0.15 mg. sulfur per milliliter, or 150 p.p.m.   A 200-ml. sample is set aside, and a series of dilution standards is made whose concentrations are 150, 120, 100, and 80 p.p.m.   150 ml. of each dilute standard is placed in a 200-ml. volumetric flask, and to each is added 25 ml. of a solution made by dissolving 120 g. sodium chloride (c.p.) and 10 ml. concentrated hydrochloric acid to make 500 ml. solution.   The flasks are shaken and made up to exactly 200 ml. with distilled water.   The first standard is then poured into a 250- or 300-ml. Ehrlenmeyer flask and shaken for 1 minute with about 1 g. of c.p. barium chloride, which is in the form of 20- to 30-mesh crystals.   The milky solution is poured into the clean cell of the turbidimeter, the lamp is adjusted to 3 volts, and a series of 10 readings is made at the point where the outline of the filament disappears.   These millimeter readings should not differ by more than a few per cent if precautions are taken to accustom the eye to the field of the instrument.   It is good practice to raise the upper tube until the filament is barely visible, then close the eye for a second.   If the filament is visible after the eye is reopened, the tube is raised a bit further and the process is repeated.   This eliminates the "imagination" factor which often causes high readings.   Each standard is read in this way, immediately after precipitation is accomplished, and the readings are plotted against the parts per million of sulfur in the 200-ml. sample, *i.e.*, after correcting for the 50 ml.-dilution.

The sulfur concentration of an unknown is then measured and reported.

2. The foregoing experiment may be duplicated with other instruments and by simple comparisons in Nessler tubes. It may be necessary to alter the concentrations given, in order to obtain readings within the range of the instrument employed.

The Nephelometer.—1. Determine either acetone, phosphorus, or sulfate by one of the methods given by Yoe and Kleinmann.[56] A photoelectric nephelometer is most suitable for student work, but the sensitivity and delicacy of nephelometric work renders all but the simplest determinations unsuitable for student instruction in a brief course.

2. A simpler alternative is the comparison of the sulfate solutions prepared above. These may be diluted somewhat if necessary prior to precipitation and compared with an intermediate standard in a Duboscq nephelometer. A working curve is constructed as directed in Sec. 74 and, if feasible, the Kober constant is evaluated. For very dilute solutions, it may be necessary to add 1 cc. 5 per cent sulfate-free gelatin for every 25 cc. of sulfate solution (see Yoe and Kleinmann[56]).

The Fluorophotometer.—1. If time permits, the student should carry out the determination of riboflavin, using the method of Hennessy and Cerecedo.[84] An alternative experiment is the determination of aluminum by the method of White and Lowe.[81] Owing to the instability of riboflavin solutions, the determination is not particularly well adapted for student work, although it is an excellent illustration of the principal use of the fluorophotometer. If aluminum standards are prepared from sodium alum for the alternative experiment, they cannot be kept for more than a week even in Pyrex bottles.

2. A less involved experiment is the determination of quinine in dilute sulfuric acid by means of a photoelectric or Duboscq fluorophotometer. Standards are prepared by diluting a quinine sulfate solution to concentrations of 0.1 to 5 mg./liter. These keep quite well. The fluorescence is bright blue and is isolated by a Corning 038 and Corning 556 combination filter.

PROBLEMS

1. An aqueous solution of colored solute is placed in a tall graduated cylinder illuminated from below and viewed from the top. Colorless dis-

tilled water is slowly poured in.   Will the hue and brightness necessarily be altered?   Discuss.

2. A solution known to obey Beer's law shows a transmission of 0.80. Calculate the transmission when

    a. The concentration is doubled.

    b. The length of the column of liquid is doubled.

3. *a.* Referring to Kober's formula, what is the significance of a negative value of K?   Of a positive value?

    b. If $c = 5$, $c_o = 10$, $Y = 10$, and $S = 20$, what is K?   What does this indicate?
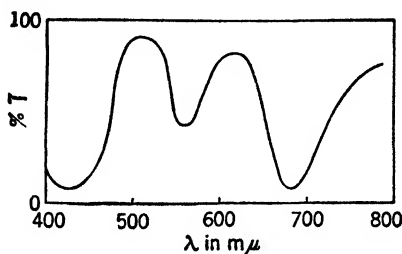
Fig. 142.

4. A colored solution yields the spectrophotometric curve shown in Fig. 142.   What should be the central wave length of a filter used for

    a. Visual colorimetric determination with a one-solution colorimeter?

    b. Photoelectric photometric determination with a one-solution colorimeter?

5. Can the specific extinction k be determined by means of a Duboscq colorimeter?   By means of a one-cell photometer such as the neutral-wedge instrument?   Explain.

6. The following data are obtained with a Duboscq colorimeter on a series of standard colored solutions of concentration c, when the cup is set at 20 mm. depth.   The concentration of the reference solution is 1 mg./liter. The Y readings are the depth of the reference solution.

c, mg./cc.	Y, mm.
1.0	20.0
1.9	41.1
2.0	43.2
2.8	62.0
4.0	90.0

    a. Is Beer's law obeyed?

    b. What is the value of Kober's constant?

    c. Is Kober's constant actually a constant?

    d. Plot a working curve of Y vs. c or R.

    e. Does this coincide with the curve predicted by Beer's law?

7. Give a nonmathematical, common-sense explanation of why a very turbid solution of relatively large particles would not be expected to obey Beer's law,

8. Two suspensions have the same "concentration," but one is composed of much smaller particles than the other. Which would show the larger transmission? (Note possible effect of other factors.)

9. A uniform suspension of absolutely white particles appears bluish when viewed at right angles to the illuminating beam. Why? What would be the transmitted hue?

10. An industrial laboratory wishes to devise rapid-control methods for analysis of a colorless filtered product with an aqueous base. It is desired to control the clarity, the copper content, which ranges from 0.008 to 0.04 mg./ml., and the vitamin B_1 content, which ranges from 0.00 to 0.003 mg./ml. After consulting the literature, draw up a report stating your recommendations. Emphasize factors of significance in an industrial laboratory, such as cost of equipment, speed, and training of operator. Assume absence of interfering constituents.

11. Explain concisely the functions of filters in

    a. Colorimetry with a two-cell colorimeter (Duboscq).

    b. Colorimetry with a visual one-cell photometer.

    c. Colorimetry with a photoelectric one-cell photometer.

    d. Nephelometry.

    e. Fluorophotometry.

12. What is the purpose of the HCl-NaCl solution used in the turbidimetric determination of sulfate as $BaSO_4$?

13. If solutions of substances such as gelatin show a Tyndall cone, how can they be used as protective colloids for nephelometry?

14. Contrast and compare turbidimetry with nephelometry, state general advantages, disadvantages, etc.

REFERENCES

1. J. H. Yoe and T. B. Crumpler, *Ind. Eng. Chem. Anal. Ed.*, **7**, 78 (1935).
2. W. R. Brode, *J. Am. Chem. Soc.*, **46**, 581 (1924).
3. J. W. Lovibond, "Measurement of Light and Color Sensations," George Gill and Sons, London.
4. J. H. Yoe, "Photometric Chemical Analysis," Vol. I, John Wiley & Sons, Inc., New York, 1928.
5. F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Company, Inc., New York, 1936.
6. W. D. Armstrong, *Ind. Eng. Chem. Anal. Ed.*, **5**, 300 (1933).
7. H. R. Wirth, *ibid.*, **7**, 147 (1935).
8. R. F. McCrackan, H. E. Harman, and E. Passamaneck, *Arch. Path. Lab. Med.*, **3**, 227 (1927); *J. Chem. Education*, **3**, 416 (1926); **3**, 928 (1926).
9. M. Winkler, *Chem. Ztg.*, **56**, 86 (1932).
10. H. Ginsberg, *Z. anorg. allgem. Chem.*, **207**, 105 (1932).
11. American Instrument Co., *Bull.* 1025, 1938.
12. P. A. Clifford and B. A. Brice, *Ind. Eng. Chem. Anal. Ed.*, **12**, 218 (1940).
13. See catalogues of Corning Glass Works and Eastman Kodak Company; see also reference 12.

14. Bausch & Lomb Optical Company, "The Exton Junior Scopometer," Rochester, N. Y.
15. E. LEITZ, Pamphlets A to F, 1937.
16. M. G. MELLON, *Ind. Eng. Chem. Anal. Ed.*, **9**, 51 (1937); **11**, 80 (1939).
17. C. ZEISS, *Z. Instrumentenk*, **35**, 35, 61, 109, 521 (1925).
18. C. SHEARD and A. H. SANFORD, *Am. J. Clin. Path.*, **3**, 405 (1933); *J. Lab. Clin. Med.*, **14**, 558 (1929).
19. R. H. MÜLLER, *Ind. Eng. Chem. Anal. Ed.*, **11**, 1 (1939).
20. H. M. PARTRIDGE, *ibid.*, **2**, 207 (1930).
21. R. H. MÜLLER, *ibid.*, **7**, 223 (1935); **11**, 1 (1939).
22. H. E. IVES and E. F. KINGSBURY, *J. Optical Soc. Am.*, **21**, 541 (1931).
23. C. ZINZADZE, *Ind. Eng. Chem. Anal. Ed.*, **7**, 281 (1935).
24. M. G. MELLON, *ibid.*, **11**, 80 (1939).
25. N. STRAFFORD, *Ann. Reports Chem. Soc. (London)*, **33**, 456 (1936).
26. R. B. WITHROW, C. L. SHREWSBURY, and H. R. KRAYBILL, *Ind. Eng. Chem. Anal. Ed.*, **8**, 214 (1936).
27. K. A. EVELYN, *J. Biol. Chem.*, **115**, 63 (1936).
28. K. A. EVELYN and A. J. CIPRIANI, *ibid.*, **117**, 365 (1937).
29. W. H. SUMMERSON, *ibid.*, **130**, 149 (1939).
30. American Instrument Co., *Bull.* 1025, 1938.
31. H. H. WILLARD, *Ind. Eng. Chem. Anal. Ed.*, **12**, 287 (1940).
32. R. A. SULLIVAN and L. C. NORRIS, *Ind. Eng. Chem. Anal. Ed.*, **11**, 535 (1939).
33. K. S. GIBSON, *Instruments*, **9**, 309, 335 (1936).
34. B. LANGE, *Chem. Ztg.*, **62**, 737 (1938).
35. L. S. ORNSTEIN, W. J. H. MOLL, and H. C. BURGER, "Objective Spektralphotometrie," Friedrich Vieweg & Sohn, Brunswick, Germany, 1932.
36. J. H. YOE and T. B. CRUMPLER, *Ind. Eng. Chem. Anal. Ed.*, **7**, 281 (1935).
37. Association of Official Agricultural Chemists, "Official and Tentative Methods of Analysis," Washington, D. C., 1940.
38. Various publications of the American Society for Testing Materials.
39. W. E. THRUN, *Ind. Eng. Chem. Anal. Ed.*, **2**, 8 (1930).
40. W. M. MURRAY and S. E. Q. ASHLEY, *ibid.*, **10**, 1 (1938).
41. F. FEIGL, "Qualitative Analysis by Spot Test," Nordeman Publishing Co., Inc., New York, 1937.
42. J. H. YOE and L. A. SARVER, "Organic Analytical Reagents," John Wiley & Sons, Inc., New York, 1941.
43. I. MELLAN, "Organic Reagents in Inorganic Analysis," P. Blakiston's Sons & Company, Inc., Philadelphia, 1941.
44. A. HILGER, *J. Sci. Instruments*, **12**, 172 (1935).
45. R. L. McFARLAN, J. W. REDDIE, and E. C. MERRILL, *Ind. Eng. Chem. Anal. Ed.*, **9**, 324 (1937).
46. A. R. NEES, *ibid.*, **11**, 142 (1939).
47. S. W. PARR and W. D. STALER, *ibid.*, **3**, 66 (1931).
48. R. T. SHEEN, H. L. KOHLER, and E. M. Ross, *ibid.*, **7**, 262 (1935).
49. J. R. BAYLIS, *ibid.*, **18**, 311 (1926).
50. W. OLSZEWSKI, *Chem. Ztg.* **50**, 694 (1926).

51. E. W. Toepfer and P. W. Boutwell, *Ind. Eng. Chem. Anal. Ed.*, **2**, 118 (1930).
52. A. W. Thomas and A. Frieden, *J. Am. Chem. Soc.*, **45**, 2522, (1923); *J. Chem. Education*, **2**, 323 (1925).
53. H. E. Schweyer, *Ind. Eng. Chem. Anal. Ed.*, **9**, 211 (1937).
54. E. T. Bartholomew and E. C. Raby, *ibid.*, **7**, 68 (1935).
55. P. V. Wells, *Bur. Standards Sci. Paper*, 367 (1920).
56. J. H. Yoe and H. Kleinmann, "Photometric Chemical Analysis," Vol. II, John Wiley & Sons, Inc., New York, 1929.
57. P. A. Kober and G. Egerer, *J. Am. Chem. Soc.*, **37**, 2373 (1915).
58. W. M. Marriott, *J. Biol. Chem.*, **16**, 289 (1913).
59. J. Grant and J. H. W. Booth, *J. Sci. Instruments*, **10**, 106 (1933).
60. J. T. W. Marshall and H. W. Banks, *Proc. Am. Phil. Soc.*, **54**, 180 (1915).
61. W. G. Exton, *Arch. Path. Lab. Med.*, **5**, 49 (1928).
62. Bausch & Lomb Optical Company, "The Exton Junior Scopometer," Rochester, N. Y.
63. Bausch & Lomb Optical Company, "The Photoelectric Scopometer," Rochester, N. Y.
64. C. D. Ingersoll and R. E. Davis, *Ind. Eng. Chem. Anal. Ed.*, **2**, 248 (1930).
65. A. B. Cummins and M. S. Badollet, *ibid.*, **5**, 328 (1933).
66. F. W. Zerban, L. Sattler, and I. Lorge, *ibid.*, **7**, 157 (1935) *et seq.*
67. P. A. Kober and S. S. Graves, *Intern. Clinics 24th Survey*, **3**, 106 (1914).
68. J. W. Ryde and B. S. Cooper, *Proc. Roy. Soc. (London) A*, **131**, 451, 464 (1931).
69. P. V. Wells, *Chem. Rev.*, **3**, 331 (1927).
70. J. Tyndall, *Proc. Roy. Soc. (London)*, **108** (1869).
71. Lord Rayleigh (J. W. Strutt), *Phil. Mag.*, **41**, 107 (1871).
72. P. Rona and C. V. Eweyk, *Biochem. Z.*, **149**, 176 (1924).
73. C. E. White, *Ind. Eng. Chem. Anal. Ed.*, **11**, 63 (1939).
74. D. B. Hand, *ibid.*, **11**, 306 (1939).
75. H. Gotó, *Science Repts. Tôhoku Imp. Univ.*, **29**, 204 (1940).
76. H. Gotó, *Chem. Abstracts*, **34**, 6895 (1940); **35**, 1720 (1941).
77. P. W. Danckwortt, "Lumineszenze Analyse," Akademische Verlagsgesellschaft m.b.H., Berlin, 1934.
78. M. Haitinger, "Die Fluoreszenzanalyse in der Mikrochemie," E. Haim and Co., Vienna and Leipzig, 1937.
79. G. C. Supplee, R. C. Bender, and O. G. Jensen, *Ind. Eng. Chem. Anal. Ed.*, **11**, 495 (1939).
80. B. Josephy, *Acta Brevia Neerland, Physiol. Pharmacol, Micro. Biol.*, **4**, 46 (1934).
81. C. E. White and C. S. Lowe, *Ind. Eng. Chem. Anal. Ed.*, **12**, 229 (1940).
82. F. H. Cohen, *Rec. trav. chim.*, **54**, 133 (1935).
83. F. Kavanagh, *Ind. Eng. Chem. Anal. Ed.*, **13**, 108 (1941).
84. D. S. Hennessey and L. R. Cerecedo, *J. Am. Chem. Soc.*, **61**, 179 (1939).

85. W. Prodinger, "Organic Reagents Used in Quantitative Inorganic Analysis," Elsevier Publishing Co., Inc., New York, 1940.
86. I. G. Priest, *Bur. Standards Research Paper*, **15**, 529 (1935).
87. B. Demarest, *Ind. Eng. Chem. Anal. Ed.*, **13**, 374 (1941).
88. F. Müller, "Physikalische Methoden der Analytischen Chemie," (W. Bottger ed.), Akademische Verlagsgesellshaft m b H , Leipzig, 1939.
89. R. W. Wood, "Physical Optics," The Macmillan Company, New York, 1934
90. I. M. Kolthoff and H. A. Laitinen, "pH and Electro Titrations," John Wiley & Sons, Inc., New York, 1941.
91. F. W. Zerban and L. Sattler, *Science*, **86**, 501, 1937.
92. W. S. Hoffman, "Photelometric Clinical Chemistry," William Morrow & Co , Inc., New York, 1940.
93. H. Freund, "Colorimetry: Its Applications in Analytical and Clinical Practice," E. Leitz, London, 1932.

CHAPTER IV

THE MICROSCOPE

98. The *compound microscope* consists of a lens or combination of lenses called the *objective* (Figs. 143 and 144) which forms a real image of the object, and a second lens or combination of lenses known as the *ocular*, which acts as a simple magnifier whose object is the real image formed by the objective.

Conventionally, the two lenses are mounted in a telescoping *body tube*, of which the upper sliding part is called the *draw tube*. The distance between the top of the ocular and the top of the brass objective frame is the *mechanical tube length*. The object, on the *stage*, is illuminated by converging light that has been reflected from a mirror and passed through a concentrating lens, or *condenser*. Focusing is accomplished by a rack-and-pinion movement for coarse adjustment, and a lever, cam, or micrometer screw for fine adjustment.

99. Magnification.—The magnification of the ocular is readily found by using the conventional formula for a simple magnifier

$$\frac{\text{Projection distance}}{\text{Focal length}} = \text{magnification} = \frac{250 \text{ mm.}}{F_e}$$

where F_e is the focal length of the eyepiece, or ocular.

The magnification of the objective, however, obviously depends on the distance between the real image and the upper focal plane of the objective, *i.e.*, upon the *optical tube length* (Fig. 143), and this is not measured in most cases. An approximate magnification may be calculated by assuming the optical and mechanical tube lengths to be equal and the object to be very close to the lower focal plane of the objective. On this basis, if the conventional mechanical tube length of 160 mm. is used, the magnification of the objective is given by the formula

$$\frac{\text{Image distance}}{\text{Object distance}} = \frac{160}{F_o} = \text{magnification}$$

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where F_o is the focal length of the objective.   In practice, the
optical and mechanical tube lengths are approximately equal
only for low-power objectives, and the preceding formula is
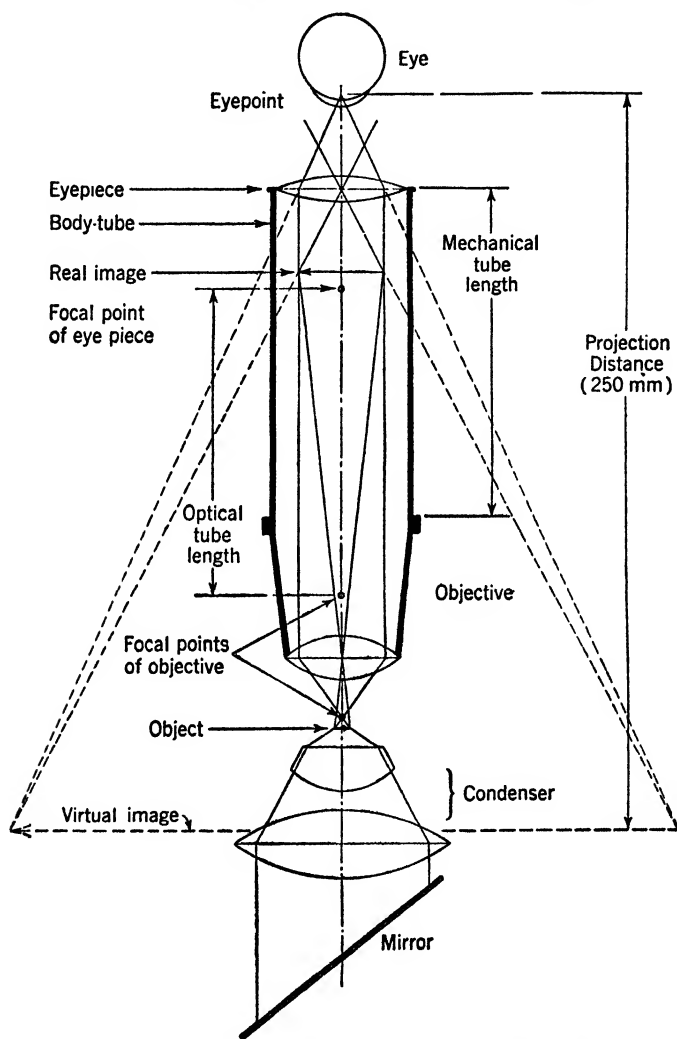
Fig. 143.—Path of rays through microscope (simplified).

therefore merely a rough guide.   To obtain a precise value, it is
necessary to determine the magnification of the objective experi-
mentally, *e.g.*, as follows: By using a standard $10\times$ eyepiece,

with the mechanical tube length adjusted to 160 mm. on the draw-tube scale, focus the objective on a stage micrometer (Fig. 145). Remove the eyepiece, and substitute a $10\times$ positive ocular micrometer with 0.1-mm. divisions, Fig. 150. Do not change the focus of the objective, but raise or lower the draw tube
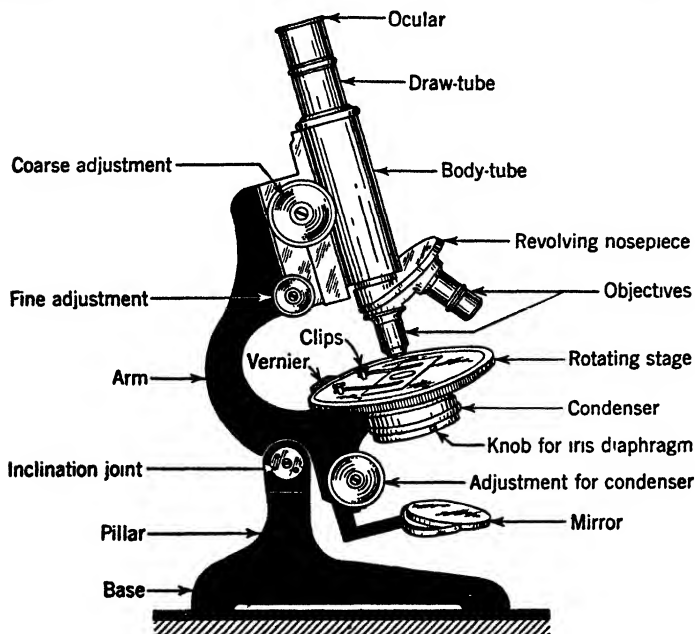
FIG. 144.—Nomenclature of parts of microscope.

0.1 and 0.01 mm
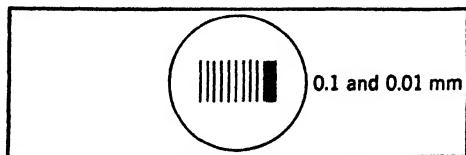
FIG. 145.—Stage micrometer.

until the stage micrometer is in focus. Move the stage micrometer until the zero mark of the ocular micrometer coincides with one of the large divisions of the stage scale and the opposite end of the ocular scale extends into the 0.01-mm. markings of the stage micrometer. Obtain the ratio of the two scales:

$$\frac{\text{Mm. on ocular scale}}{\text{Mm. on stage micrometer}} = \text{magnification of objective alone}$$

The magnification of the *microscope* for a tube length of 160 mm. will then be given by the relation

Total magnification = magnification of ocular × magnification of objective

100. Resolving Power.—Beyond a certain point, the power of the microscope to reveal details depends less on the magnification and more on the clarity or sharpness of the image produced by the objective. Excessive magnification by the ocular of a poorly defined image is obviously futile; hence, at high magnification, the *resolving power* of the objective is of greatest importance. Resolving power is loosely defined as the ability of an objective to reveal the fine structure of an object, or more precisely as the ability to distinguish two lines separated by r cm. The resolving power is also expressed as the reciprocal of r, *e.g.*, the number of lines per centimeter or inch denoted by R.
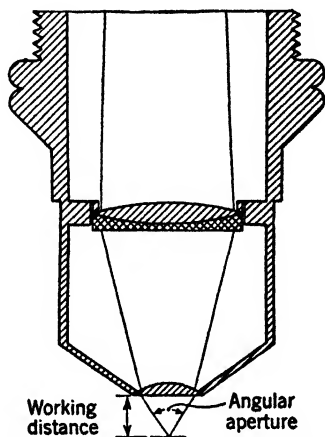
FIG. 146.—Low-power objective.

101. Aperture of Objective— Resolving Power.—The angle between the most divergent rays that can pass through an objective is called the *angular aperture* of the objective (Fig. 146). Obviously, the larger this angle, the more light enters the lens system, and the more brilliant the field of the microscope. It is customary to express the aperture of an objective in terms of the sine of this angle

$$\text{Numerical aperture} = n \times \text{sine}\left(\frac{\text{angular aperture}}{2}\right) \cong \frac{d}{2f}$$

where n is the refractive index of the medium between the objective and the object. (n is 1.0 in the case of air.) If several media are present, then n refers to the *lowest* refractive index shown by any substance between the objective and the object. If n is large, obviously the numerical aperture of the objective is increased, and the field of view of the microscope is more

brilliantly illuminated. The effective aperture of the rear lens of the objective is denoted by d; f is the focal length of the objective.

The resolving power of a lens is governed by its numerical aperture according to the equations

$$R \cong \frac{N.A.}{\lambda} \qquad \text{For parallel illumination}$$

$$R \cong \frac{2N.A.}{\lambda} \qquad \text{For oblique illumination and convergent illumination}$$

where λ is the wave length of the illuminating light (average 5,600 A for white light). From this it follows that the resolving power R increases as

1. Wave length decreases (toward violet).
2. n increases (immersion objectives, Sec. 112).
3. Numerical aperture increases.

For ordinary daylight illumination, the resolving power of an objective is approximately $100,000 \times (N.A.)$ lines to the inch, or $40,000 \times (N.A.)$ lines per centimeter.

Recent developments in methods of focusing[23,24] have led to the belief that the resolving power of a photomicrographic system is considerably better than that calculated on the basis of the preceding equation and that the actual depth of focus of an objective is far less than that claimed by the makers.

It should be borne in mind that the use of light of low wave lengths, or immersion media, to increase numerical aperture is not without certain disadvantages. The eye does not function particularly well for deep blue or violet light, and for visual microscopy it is well to use yellow-green illumination rather than light of shorter wave length. Further, the use of immersion liquids (Fig. 151) is more or less restricted by the character of the objective. Certain objectives are corrected for use in air, and if an immersion liquid is used, these corrections are no longer perfect. On the other hand, some objectives are specifically designed for use with immersion media and will not function properly in air. The immersion liquid is usually specified by the maker of the objective and is commonly cedarwood oil ($n = 1.52$) or some synthetic substitute. Other immersion media are water ($n = 1.33$) and glycerin ($n = 1.46$). A small

drop of medium is placed on the cover glass and the objective is gently lowered until it is in contact.

102. Brilliance or Illuminating Power.—The brightness of the field of view of an objective depends on the numerical aperture in accordance with the general relation that the illuminating power is proportional to the square of the numerical aperture. It is obviously impossible to give an equation that will apply to all kinds of objectives under all conditions, and this proportion applies only in a relative sense.

103. Working Distance and Depth of Focus.—The working distance of an objective is the distance between the front lens and an object which is in focus. (Fig. 146.) Since an objective is not a simple thin lens, the working distance is not even approximately equal to the focal length. For low-power objectives, the working distance is frequently larger than the focal length of the objective, but for medium- and high-power objectives, the working distance is between one-half and one-tenth of the focal length (see Table 10). In general, placing a cover glass between the objective and the object decreases the working distance by two-thirds of the thickness of the cover glass.* The working distance is unusually small for apochromatic objectives (see Table 10).

The *depth of focus*, or penetrating power, of a lens is the maximum separation of two planes that are both apparently in sharp focus, although not equidistant from the lens. A large depth of focus is obviously a very desirable property of an objective, since it permits the microscopist to see various strata in a microscopic specimen, without the necessity of continually refocusing the microscope. The depth of focus varies approximately as the square of the focal length and inversely with the numerical aperture

$$\text{Depth of focus} \propto f^2 \propto \frac{1}{\text{N.A.}} \qquad \text{(see Table 10)}$$

104. Types of Objectives.—Objectives are generally classed according to magnification, numerical aperture, and degree of optical correction, and also as "dry" or "immersion."

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* Cover glasses are graded according to thickness:

No. 1.................................... 0.15 mm.
No. 2.................................... 0.2 mm.
No. 3.................................... 0.25–0.35 mm.

Table 10.—Characteristics of Objectives*

Type	Magnification	f, mm.	N.A.	Working distance, mm.	Diameter of field (10× neg. ocular), mm.
Apochromatic:					
Dry..................	10	16	0.30	4.85	1.50
	20	8.3	0.65	0.50	0.76
	45	4	0.95	0.18	0.31
Oil immersion.........	61	3	1.4	0.12	0.25
	90	2	1.30	0.12	0.16
	90	2	1.40	0.07	0.16
	120	1.5	1.30	0.08	0.12
Achromatic:					
Dry..................	4	32	0.10	38.0†	3.87
	10	16	0.25	7.0†	1.50
	21	8	0.50	1.6†	0.74
	43	4	0.65	0.60†	0.35
	43	4	0.85	0.30†	0.35
Water immersion......	44	4	1.0	0.64	.....
Oil immersion.........	80	2.2	1.25	0.20†	0.185
	97	1.8	1.25	0.13	0.15
Fluorite:					
Dry..................	43	4	0.85	0.34	0.35
Oil immersion.........	40	4.3	1.0	0.27	0.37
	98	1.8	1.30	0.13	0.155

* Excerpts from Bausch & Lomb Catalogue D111.
† Objectives which find most frequent use in chemical microscopy and petrography.

The degree of optical correction is a more or less arbitrary classification into three groups:

1. Aplanatic—Corrected for axial spherical aberration, astigmatism, and coma (distortion by unequal magnification of different parts of field, etc.).

2. Achromatic—Corrected for chromatic aberration (two colors). Also generally aplanatic.

3. Apochromatic—Corrected for chromatic aberration (three colors). Usually very fine lenses of high numerical aperture. Require the use of compensating oculars to correct for the slight differences in magnification for different colors.

In addition to the preceding classes, there is an intermediate group known as semiapochromatic or "fluorite" objectives.

These employ a lens of calcium fluoride, together with the usual glass lenses, and are not used with polarizing microscopes, since fluorite is "optically anisotropic."

The differences among the various types of objectives is quite noticeable, and it is important for the microscopist to choose objectives that will perform the task he requires. For chemical work, the requirements are especially harsh, since the chemical microscopist has to make a great variety of observations. A general survey of microchemical and petrographic demands might be as follows:

1. For low-power work in general, observation of drop reactions, etc.: Most objectives are suitable; long working distance is especially desirable (8 mm., 16 mm. achromatic). For photomicrography, special corrections are needed to ensure flatness of field.

2. For high-power ($>200\times$) work in general: Choice must be made between high resolving power and long working distance. Apochromats are especially desirable for examination of fine structure and when observations of color are necessary but have the great disadvantage of a small working distance (4-mm. dry achromat, 2-mm. oil-immersion apochromat).

3. For polarizing microscope: Long working distance and great depth of focus are desirable in 4- and 16-mm. objectives, which should be achromats. A high N.A. 2-mm. immersion objective with suitable condenser is convenient for examination of interference figures. Lenses should be strainless and of isotropic material (not fluorite, etc.).

105. Testing Objectives.—One of the simplest and most practical methods is that suggested by Chamot and Mason.[2] They recommend a slide of finely divided white pigment (dry paint pigment such as Titanox) whose particles are 0.2 to 1 μ (1 micron-0.001 mm.) in diameter. The pigment is dusted very thinly on the slide and is examined under a variety of conditions of illumination. Absence of color fringes and blurred images indicates a good objective. Depth of focus and curvature of field are readily ascertained, and the resolving power of the objective may be estimated. This test should be made on a series of objectives of various types in order to appreciate the really great differences in degree of correction and resolving power.

The historical test for the perfection of a lens system is the ability to resolve the fine structure of certain diatoms, notably *Amphipleura pellucida.* A similar and more reproducible set

of test objects is a series of gratings of 40,000 to 120,000 rulings to the inch.   (The latter are not readily available, however.)

The Abbe test plate is also used for testing the degree of correction.   This is simply a microscope slide with three mounts under cover glasses of different thickness.   Each mount consists of a small mirror whose silver surface has been cut in parallel bars by ruling with a wooden point.   The test is simply the observation of any fringes or colored halos at the edges of these bars.

106. Cover-glass Correction.—Objectives of high magnification and large numerical aperture are corrected for use with cover glasses of definite thickness.   This fact is illustrated best by the Abbe test plate,[3] but even the above-mentioned test with particles of pigment will show the difference between a cover glass of the correct thickness and one for which the objective is not corrected.   Some objectives are equipped with a rotating collar which permits a slight movement of the components of the objective in order to compensate for the thickness of the cover glass.
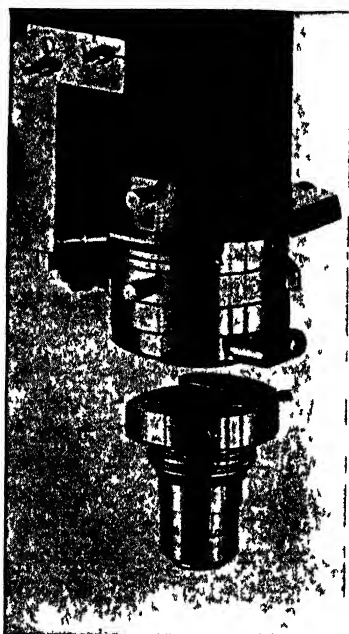
Fig. 147.—(*Courtesy of Bausch & Lomb Optical Company.*)

107. The Nosepiece.—The nosepiece provides for rapid interchange of objectives.   A rotating device (Fig. 144), which is attached to the body tube, accommodates from two to four objectives and may be so constructed that upon shifting from one objective to the other the focus is not impaired.   In this case, the nosepiece is said to be *parfocal*.   Another type of nosepiece is known as the sliding, or clutch-interchanging, type and involves the use of a grooved plate and locking slot, attached to the body tube (Fig. 147).   A similar plate is permanently attached to the objective by means of a threaded tube.   In use, the objective plate is placed in contact with the body-tube plate and locked in position.

By means of accurate construction and the use of centering screws, it is possible to obtain parfocalization and reproducible, perfect centering.

THE EYEPIECE OR OCULAR

108. Function of the Ocular.—The ocular has a twofold purpose: it acts as a simple magnifier for the real image formed by the objective, and it usually corrects for some residual aberrations of the objective. This latter is especially true of the compensating ocular, mentioned previously, which corrects the real image formed by an apochromatic objective for differences in magnification for different colors.

Oculars are generally lenses of low numerical aperture, and for most work those having magnifications between 5× and 15× are most satisfactory. The only requirement of an ocular is that it do justice to the real image formed by the objective and, owing to the relatively large size of this image, the requirement is easily met.

109. The Eye Point.—This is best defined as that point above the ocular where the eye naturally and automatically is placed in order to see the image. Actually, the eye point is a small circle that includes rays coming from the entire field of the microscope (Figs. 148 and 149). The diameter of this circle depends on the aperture of the objective and condenser, on the magnification of the microscope as a whole, and on the diameter of the diaphragm in the ocular. If the microscope is

FIG. 148.—Negative ocular (Huygenian).

illuminated sufficiently, it is possible to see the eye point on a piece of ground glass or tracing cloth held above the ocular. The height of the eye point above the eye lens of the ocular depends on the focal length or magnification of the ocular itself. This fact imposes a definite limit on the magnification of the ocular, since for high-power oculars the eye point may be uncomfortably close

to the lens.   Oculars have been designed which give an eye point well above the eye lens, so that persons with spectacles can see the entire field of view without pressing against the eyepiece.

110. Types of Oculars.—The two types of ocular in common use are the negative *Huygenian* and the positive *Ramsden*.   The negative ocular (Fig. 148) consists of two plano-convex lenses, the lower or *field lens* having about half the focal length of the
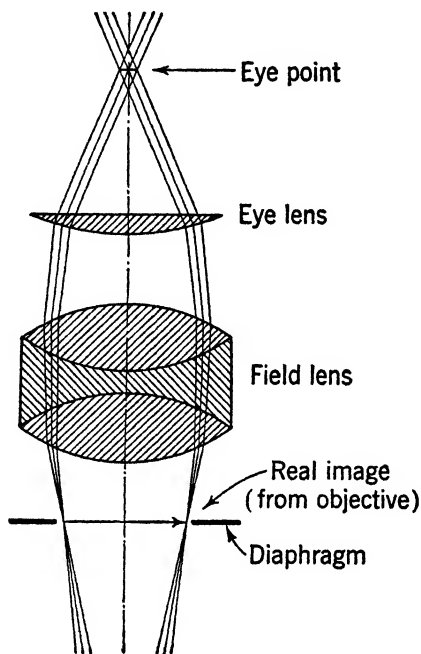
Fig. 149.—Positive ocular (Ramsden).

eye lens.   The two lenses are separated by a diaphragm which is in the plane of the real image.   The diameter of the field of view of the ocular is limited by the size of this diaphragm and by the focal length of the field lens.   Note that this field lens serves to *reduce* the size of the real image and hence to *increase* the diameter of the field of view.   Huygenian oculars are most commonly used in general work, both in the simple form illustrated and with the substitution of compound lenses.   For chemical work, it is best to use oculars that are equipped with cross hairs mounted in the plane of the diaphragm.

The positive ocular (Fig. 149) is distinguished from the negative ocular by the location of the real image with regard to the field lens.   If the real image from the objective is *below* the field lens, then the ocular is positive.   Positive oculars of both simple and compound types are usually used for measuring.   In this connection an etched or ruled glass scale is placed directly over the real image.   Any distortion of the image that is due to the ocular then applies equally to the scale.   Positive oculars are also used for higher magnifications, since they are more easily corrected.

Many special types of oculars are available, in addition to those mentioned.   Projection oculars, flat field oculars, micrometer oculars, and oculars of very high magnification for testing objectives are listed in manufacturers' catalogues.   Almost all oculars are corrected for chromatic aberration and flatness of field, although special types are often necessary for refined work.

111. Ocular Micrometers.—A transparent graduated scale mounted in the ocular in the plane of the real image of the objec-
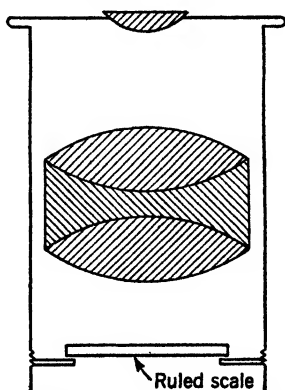
Fig. 150a.—Positive ocular   Fig. 150b.—Negative ocular
       micrometer.   micrometer.
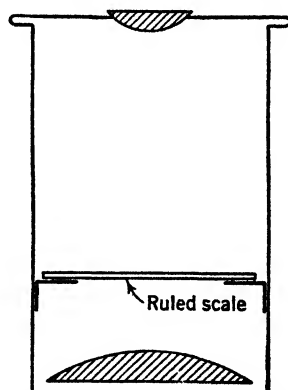
tive or the focal plane of the eye lens is called an *ocular micrometer* (Fig. 150).   The graduations are usually in tenths or twentieths of a millimeter, or in thousandths of an inch, and may be in the form of either a simple scale or a coordinate net.   A more accurate type involves two scales, one of which is attached to a traveling micrometer screw mounted outside of the ocular.   The movable scale is often a single cross hair, whence the name *filar micrometer.* Since the value of the divisions of the ocular scale in terms of the

actual distance measured on the object depends on the magnification of the microscope, it is necessary to calibrate the ocular scale against a known standard scale or *stage micrometer* (Fig. 145). These stage scales are customarily graduated in tenths and hundredths of a millimeter or in thousandths of an inch.

THE CONDENSER

112. The condenser is a converging lens located below the stage of the microscope, which serves to illuminate the object by concentrating and focusing the image of a light source upon it. As mentioned in Sec. 101, the degree of obliquity of the illuminating light affects the resolving power of an objective; hence the use of a strongly converging condenser should increase the resolving power of an objective. This is generally true, in accordance with the equation

$$\text{Resolving power} = R = \frac{\text{N.A. condenser} + \text{N.A. objective}}{\lambda}$$

A condenser should have a numerical aperture roughly equal to that of the objective with which it is used in order that the concentrated light at the focal plane of the condenser will fill the entire aperture of the objective. Whether or not the field is satisfactorily illuminated may be ascertained by examining the eye point above the ocular with a small hand magnifier. The back of the objective is then made visible, and if it is not at least two-thirds illuminated, the numerical aperture or focal length of the condenser is too small. The back of the objective may also be observed by removing the ocular and looking down the body tube. To eliminate the necessity of changing the condenser every time the objective is changed, separable two-lens condensers are often used, which permit the removal of the upper short-focus lens by movement of a lever or knurled knob.

113. Three types of condensers are in common use: the Abbe condenser, (Fig. 151) which has one or two uncorrected lenses; the aplanatic condenser, which is more highly corrected for flatness of field; and the achromatic condenser, corrected for spherical and chromatic aberration. The numerical aperture of these condensers varies from about 0.2, for use with 16- and 8-mm. objectives, to 1.0, for use with 4-mm. objectives. If high-magnification large numerical-aperture objectives are used, it is

necessary to use immersion oil between the condenser and the slide, as well as between the objective and the mounted object. Immersion condensers of N.A. of 1.2 to 1.4 are available.   Immersion oil *must* be used in order to realize the full numerical aperture.

It is possible to use a well-corrected condenser to project the image of a transparent scale onto the object placed on the micro-
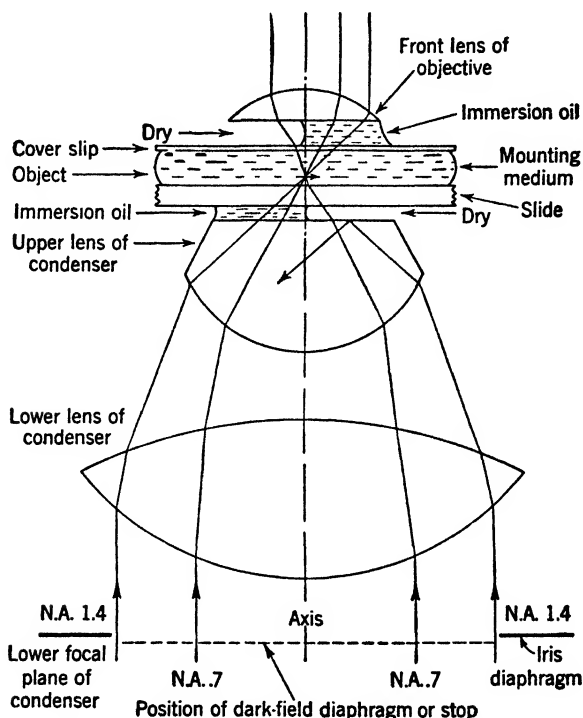
FIG. 151.—Path of rays through dry and immersion condensers.

scope stage.   The scale is attached to the light source, or the condenser diaphragm, and the image formed by the condenser is adjusted until it falls on the object under examination.

From the foregoing discussion of the use of immersion oils to increase the numerical aperture of objectives (Sec. 101), it is apparent that if an object is mounted in a medium whose refractive index is similar to that of glass, and if the objective and condenser are immersed in media of the same index, then light from the condenser will travel in a straight line to the objective,

without losses from refraction and total reflection at interfaces. Such a *homogeneous immersion* system is illustrated in Fig. 151.

The numerical aperture of any condenser may be reduced by closing the subcondenser diaphragm. This procedure, of course, darkens the field somewhat but increases the sharpness or *relief* of a gross object. *It is customary to adjust the subcondenser diaphragm until the aperture of the objective is not quite filled with light* so that both brilliance and sharpness of detail are at their optimum values.

114. Certain types of objectives act as their own condensers. The so-called *vertical illuminating* objectives (Fig. 152) include a small prism or other reflector attached either to a collar between the objective and the body tube or to the inside of the objective
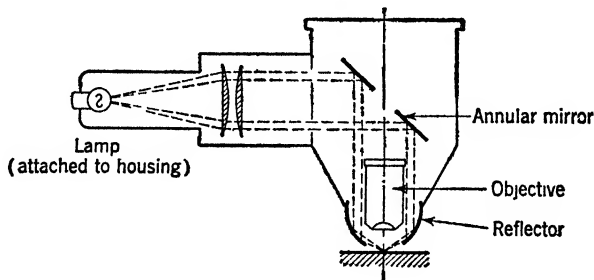
Fig. 152.—Vertical illuminator for observation of opaque objects (schematic). (*After Zeiss Epicondenser.*)

tube in such a way that light from a near-by source enters and is reflected down through the objective to the object. The reflector does not interfere with the normal function of the objective, and when the object is viewed through the eyepiece it appears beautifully illuminated against a dark background. An alternative method of illuminating opaque objects is to employ an annular mirror which fits about the objective. Light from below strikes the curved surface of the mirror and is focused by reflection on the object. The *Silverman illuminator* is a tubular incandescent bulb and reflector curved to form a circular "doughnut," which fits over the objective. The Leitz Ultropak and Zeiss Epicondenser are much more elaborate devices which are fitted between the body tube and objective and which contain an integral light source. Several modifications are available.

115. Dark-field Illumination.—If an opaque circular stop is placed just below the lower lens of a short-focus condenser so that

it intercepts only rays that would travel through the central portion of the condenser (Fig. 153), then the object will be illuminated by peripheral rays only, and under proper conditions no direct light will enter the objective. The result is the pleasing effect of a glowing object against a black field. (It is claimed that this type of illumination increases the resolution of the microscope.) A similar but more striking effect is obtained if the opaque stop is replaced by a colored filter and the annular space between the filter and the rim of the iris is occupied by a filter of another color. The object then appears of one color and the
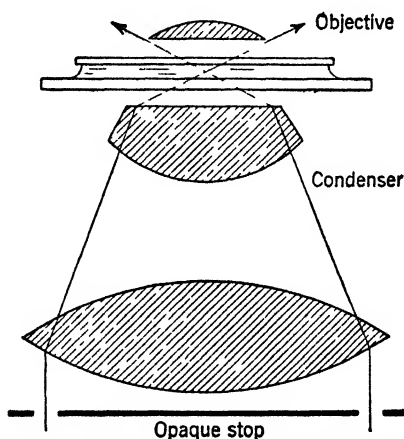
Fig. 153.-- Path of rays in dark-field illuminator.

field of a different color. In either case, it is necessary to adjust the numerical aperture of the condenser to suit that of the objective and the size of the stop to completely eliminate rays that would be transmitted by the objective.[3]

Dark-field effects may sometimes be secured by shielding one side of the condenser with a piece of cardboard, so as to obtain highly oblique illumination, or the object may be illuminated from the side with a bull's-eye light, which is a short-focus convex lens held at a distance from a concentrated filament lamp. An even simpler but not so satisfactory expedient is to remove the condenser entirely and swing the mirror to one side in such a manner that light reflected from the concave side of the mirror illuminates the object but not the objective.

ILLUMINATION

116. For general work at low magnifications, daylight (not direct sunlight) or light from a frosted blue-glass electric lamp is sufficient. Several types of inexpensive microscope illuminators are listed by microscope dealers, which usually employ a 10-watt 110-volt bulb backed by a reflector and with a correcting filter of Daylite glass. One disadvantage inherent in these illuminators is the small diameter of the beam produced. In order to illuminate the entire aperture of the microscope, it is
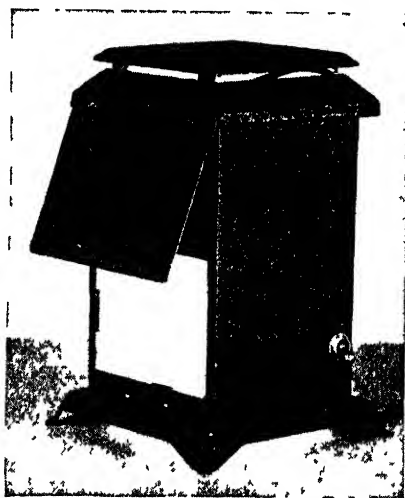
Fig. 154.—Modified chalet lamp.   (*Courtesy of Spenser Lens Company.*)

frequently necessary to move the lamp close to the condenser, which may result in undesirable heating of the latter. Gage[3] recommends a modified illuminator consisting of a lighttight ventilated box with ground Daylite glass windows about 3 in. square (Fig. 154). The lamp is a clear 100-watt incandescent bulb. This illumination suffices for all magnifications up to and including 1,000×, but it is not recommended for use with filters or for dark-field work. A 6-volt ribbon filament bulb, used with an auxiliary condensing lens, is very satisfactory for high-power work and dark-field illumination but is inferior in many respects to the capillary mercury arc, which operates on alternating current and which is adaptable to the standard screw-base socket.

The entire system (Fig 155) should be enclosed in a telescoping body, and provision should be made for the insertion of colored glass filters and a heat-absorbing cell. This latter may be a water cell or heat-absorbing glass (Corning Glass Company) Habitual use of a green filter is to be recommended because the roughly monochromatic light reduces chromatic effects in the microscope and is restful to the eyes
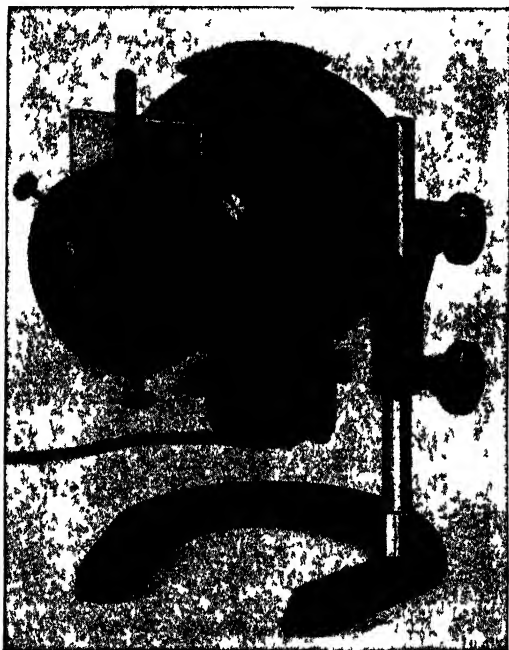
FIG 155 —Adjustable microscope lamp   (*Courtesy of Bausch & Lomb Optical Company*)

117. Monochromatic Light.—Light of a single wave length is often required in petrographic work. The best source is the mercury-vapor arc supplemented by filters that isolate the intense red, yellow, green, or blue lines of the mercury spectrum. Mercury arcs are available for both alternating and direct current.   (Recent models using alternating current are made in the form of the ordinary incandescent bulb)   The familiar sodium-vapor arc, used in some cities for street lighting, is well adapted to use as a microscope illuminator, and inexpensive sodium-vapor lamps are on the market

Prism and grating *monochromators* are available, which provide monochromatic light of any desired wave length. These have the disadvantages of expense and low intensity. Various makeshift devices have been improvised, however, whose only advantage is low cost.[2] Use of the Bunsen flame, colored by various metal salts, as a source of monochromatic light is recommended only as a temporary expedient. Fumes resulting from the colored flames are either poisonous or corrosive, and the intensity is low.

Filters are exceedingly useful and satisfactory when absolute monochromaticity is not essential. The use of liquid filters[1,25] is not to be recommended if it is possible to replace them by glass or gelatin filters (Table 11). Hartshorne and Stuart,[5]

TABLE 11.— MONOCHROMATIC LIGHT SOURCES

Source	Filter	Wave length, A	Color
Mercury arc.............. ..	C.G.* 038 C.G. 511	4,358A	Deep blue
	C.G. 351 C.G. 512 C.G. 430	5,461	Green
	C.G. 245 C.G. 428	6,234	Orange
	C.G. 241	6,908	Red (weak)
Cadmium-mercury arc........	C.G. 243	6,438	Red (intense)
Sodium arc (or flame)........	None	5,893	Yellow
Thallium flame............ .	None	5,351	Green
Lithium flame..............	None	6,708	Red
White light.................	C.G. 511	4,000–4,500	Deep blue
	C.G. 554 C.G. 038	1,500–5,000	Blue
	C.G. 401 C.G. 430	5,000–5,500	Green
	E.K.† 58 E.K. 22	5,500–6,000	Yellow
	C.G. 245 C.G. Aklo	5,900–6,500	Orange
	C.G. 241	6,400–7,600	Red

* C.G. refers to Corning Glass molded or polished filters.
† E.K. refers to Eastman Kodak Wratten filters of gelatin mounted in B glass.
For further data on these filters, see catalogue of Corning filters and pamphlet "Wratten Filters."

however, recommend the use of an 8- to 10-cm. cell containing
a mixture of 6 volumes saturated potassium dichromate solution
with 1 volume saturated copper sulfate solution. It is claimed
that this mixture gives light approximating that of the sodium
flame.

Adjustment of Illumination.—Whatever source is used, it is
desirable to focus its image directly on the object under observa-
tion. This procedure is accomplished by first focusing the
microscope on the object and then by racking the condenser
up or down until the image of the light source is seen super-
imposed on the object. Since the light source is generally
a ground-glass filter, the graininess of the surface may give
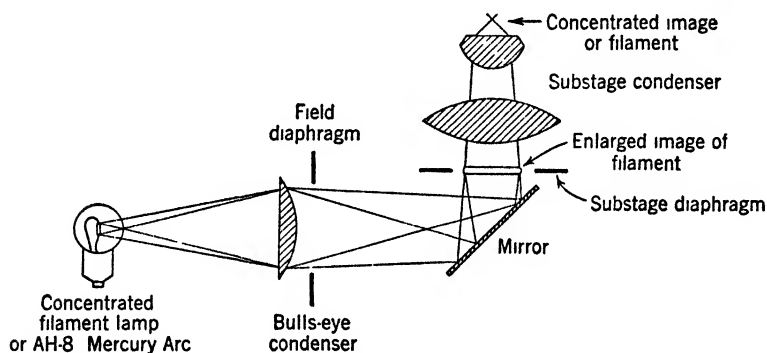
FIG. 156.—Kohler method of illumination.

an undesirable background. This is easily remedied by moving
the condenser slightly so that the image of the ground glass
is thrown just out of focus. Illumination thus achieved ensures
optimum resolution and is known as *critical illumination*. An
alternative method, which permits the use of a source of smaller
area, is due to Kohler (Fig. 156). In this method, an enlarged
image of the source is projected, by means of an auxiliary lens,
onto the lower focal plane of the condenser, which is the plane
of the subcondenser diaphragm.

Summary of Rules Regarding Illumination at High Magnification.
1. Focus microscope on object.
2. Focus condenser on object, then move slightly out of focus.
3. Remove ocular and see if rear of objective is filled with light.
4. Close subcondenser diaphragm until edge of iris is visible at rear
of objective. Reinsert ocular and proceed.

<div align="center">THE PRACTICE OF MICROSCOPY</div>

118. Preparation for Microscopic Examination.—The chemist usually has more to do with small crystals, powders, and liquids than with gross specimens, and the latter may be dismissed with the observation that sectioning with a microtome or grinding and polishing are generally necessary prerequisites to observation at moderate or high magnification. A complete description of the methods involved and an excellent collection of references is given in the text by Chamot and Mason.[2]

Small particles may be observed at low magnification without any preparation whatsoever, but for magnifications of over $100\times$, the specimens should be mounted in some suitable medium (see Sec. 119) and covered with a cover glass. The mounting medium serves a twofold purpose: it immobilizes the particles to some extent, and it helps to reduce internal reflections.

<div align="center">TABLE 12.—COMMON MOUNTING MEDIA</div>

Medium	Refractive index (approximate)	Properties
Water..................	1.33	Temporary, evaporates rapidly
Glycerin...............	1.46	Transparent to ultraviolet
Karo (sugar sirup).......	1.46	Slow-hardening, semipermanent
Nujol..................	1.47	Temporary
Isobutylmethacrylate	1.48	Permanent (polymerizes)
Canada balsam (xylene)..	1.54	Permanent
Clarite.................	1.54	Permanent
Clarite X..............	1.56	Permanent
Bromoform.............	1.57	Temporary
Styrax (xylene)..........	1.57–1.60	Permanent (like balsam)
Bromonaphthalene.......	1.66	Temporary
Styrene resin (xylene)....	1.66	Permanent
Methylene iodide........	1.74	Temporary (discolors)

A small drop of the medium is placed on the microscope slide, the sample is introduced, and, after pricking any bubbles, the cover glass is gently lowered into place by means of flat-tipped forceps. Excess sample or excess medium must be avoided. If a semipermanent or permanent mounting medium is used, the mount should be allowed to harden and then "ringed" with

enamel to seal the edges of the cover glass.　A spinning table and some heavy enamel such as Duco are generally used for the "ringing" operation.　Temporary mounts that employ less viscous media may be prepared by placing a cover glass over the dry specimen and introducing the medium at the edge of the cover glass, from which it spreads by capillary action.　In either case, it is important that no liquid touch the top of the cover glass and that only enough liquid be used to cover the specimen. Excess medium will cause the cover glass to "swim" or slide about.

Slides and cover glasses should be cleaned with acid dichromate, trisodium phosphate, or hexametaphosphate (Calgon), rinsed with distilled water and then alcohol, and dried by evaporation. Use of linty cloths or tissues should be avoided.

119. Appearance of Objects.—The degree of transparency, color, and shading of objects viewed through a microscope are seldom inherent but arise from refraction and diffraction effects. The observed transparency of a minute particle is governed to a large extent by the refractive index of the mounting medium. Thus, a particle of refractive index 1.70 may appear black and metallic when mounted in air or water, yet become transparent when mounted in monobromonaphthalene ($n = 1.66$).　The various shadings and dark outlines observed on the specimens may not indicate changes of contour but may be due to refraction.　Observations of color are also uncertain unless apochromatic lenses are employed.　In addition, some specimens will exhibit anomalous tints when immersed in a medium of similar refractive index but different dispersive power, *e.g.*, powdered glass in a mixture of nujol and bromonaphthalene whose index is 1.510.　A good general rule is to employ a mounting medium whose refractive index is about 0.05 units from that of the object to be studied (see Sec. 162).

THE USE OF THE MICROSCOPE AND ACCESSORIES—EXPERIMENTAL

120. Study the construction of the microscope, and familiarize yourself with all the various adjustments.　To focus the microscope, place a slide on the stage, and lower the body tube by means of the coarse adjustment until the front lens of the objective almost touches the cover glass.　Then focus on the specimen

by *raising* the tube. *Never focus down while looking through the microscope.* Adjust the illumination as directed in Sec. 117. Investigate the properties of several objectives and combinations of objectives and oculars. If the microscope is equipped with a rotating stage, check the centration of the stage by focusing on a small particle at the intersection of the cross hairs of the ocular. Rotate the stage 135°, and if the particle is no longer in the center
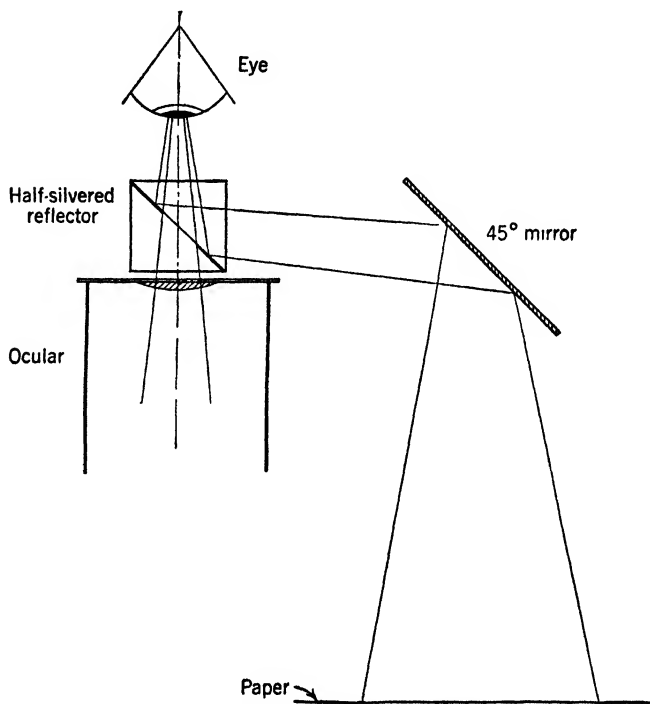
FIG. 157.—Abbe camera lucida.

of the field, adjust the centering screws of either the stage or the nosepiece until the particle has been brought back *one-half* of the way to the center. Move the slide so that the particle is again at the intersection of the cross hairs, rotate the stage 90° further in the same direction, and again bring the particle half-way back to the center. Repeat this operation at 90° intervals until the stage is centered.

To check the centration of the substage, focus the condenser, remove the ocular, and examine the back of the objective (4 mm.)

while closing the substage diaphragm. The diaphragm opening should be exactly concentric with the objective frame.

Examine a thin smear of starch grains in water with the 16- and 4-mm. objectives. (Use a cover glass.) Experiment with the illumination as follows:

1. Axial illumination--Low-power condenser stopped down and lowered.

2. Convergent illumination—High-power condenser open and focused. (It is best to use the plane side of the mirror. Note the effect of closing the substage diaphragm.)

3. Oblique illumination—Shade half the condenser with a card.

4. Dark-field illumination—Use dark-field stop of suitable diameter, and adjust the iris until the field is dark (16-mm. objective). A powerful light source should be used.

5. Examine starch grains mounted in Canada balsam and a slide of dry-mounted white pigment powder. Note the colored halos, if present, in the latter.

121. The Camera Lucida or Drawing Ocular.—This valuable accessory permits simultaneous observation of the field of the microscope and a sheet of paper placed beside the microscope so that the field appears to be superposed on the paper. The utility of such a device for tracing drawings of microscopic images is obvious. Two types of drawing oculars are shown in Figs. 157 and 158.

In practice, it is usual to balance the illumination of the microscope field and that of the paper by the use of neutral-tint dark-glass plates, which are mounted close to the prism in such a way that they may be swung into position whenever desired.
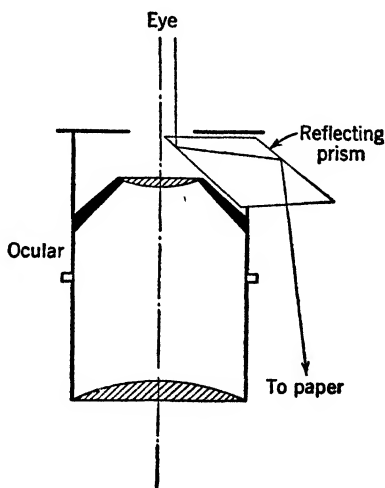
Fig. 158.—Wollaston type of camera lucida.

A factor that must be taken into account is the possible distortion of the tracing due to poor alignment of the paper with the optical axis of the drawing ocular. A tilting drawing table is

generally employed so that the paper may be adjusted to exact perpendicularity to the optical axis of the reflecting surface.

122. Determining Magnification with the Camera Lucida.— With the stage micrometer in place, remove the ocular and substitute an Abbe or Wollaston drawing ocular. Refocus if necessary, then tilt the microscope to a convenient angle and place a piece of white paper in its proper position. Trace as many micrometer lines as possible on the paper, but do not use those lines which are tangent to the edge of the field. Measure the distance between two extreme lines with a ruler. The magnification of the system is then

$$\frac{\text{Mm. between extreme lines on paper}}{\text{Mm. between corresponding lines on micrometer}}$$

This magnification value is of use if one is to trace objects on paper and then measure the tracing, but it is not the magnification of the microscope, because it obviously depends on the distance from the eye point to the paper. Since the image seen through a microscope appears to be at the distance of clear vision (250 mm.), the actual magnification of the microscope is

$$\text{Magnification of system} \times \frac{250}{\text{distance from eye point to paper}}$$

(The distance from the eye point to the paper is best measured by means of a string, which is then laid on a meter stick.)

123. The Ocular Micrometer and Stage Micrometer: Measurement of Length.—Use a $10\times$ ocular, a 4 mm. objective, and a stage micrometer. With the tube length set at 160 mm., adjust the stage micrometer so that the zero mark of the ocular scale coincides exactly with some mark of the stage micrometer scale. If the latter is ruled with fine divisions at one end, be sure that the fine divisions are at the opposite side of the field from the zero of the ocular scale. Obtain the ratio of the ocular to the stage scale by noting some point at which two marks coincide exactly. From this ratio, which should be the average of several settings, determine the value of the divisions on the ocular scale in terms of actual lengths on the stage.

Measure the thickness of a paint film, the diameter of a silver bead, etc. Note that the weight of very tiny particles may be

computed provided that the density is known. (This is actually a method of assaying low-grade ores.)

124. Measurement of Height or Depth.—In addition to measuring lengths, the microscope is capable of measuring vertical distance. Almost all modern microscopes are equipped with a graduated micrometer screw, which is used for fine focusing. This screw is usually sufficiently accurate to permit its use in precise measurements, provided that the conventional means of eliminating the effects of backlash is employed, *i.e.*, provided that the screw is always moving in the same direction when readings are made. Readings may be made to within 2 or 3 μ, and, depending on the type of microscope, power of objectives, etc., the range covered varies from 1 to 5 or 6 mm. Microscopes that employ the lever or cam action for fine focusing are also equipped with a graduated fine adjustment knob.

125. Measurement of Refractive Index of Liquids.[2,20]—The calibrated fine adjustment serves as a micrometer screw which enables the microscopist, by focusing first on the top and then on the bottom of an object, to measure height or depth as mentioned above. The example given here as an illustration of this point depends upon the fact that the apparent depth of a cell filled with liquid is less than the actual depth, the determining factor being the refractive index of the liquid in accordance with the relation

$$\frac{\text{Actual depth}}{\text{Apparent depth}} = n$$

The cell, which should be 1 to 2 mm. deep, may be constructed from a metal or plastic washer which has been ground flat and cemented to a slide. An 8 or 16 mm. objective is used.

Experimental.—By means of a fine pipette, fill a cell with liquid until a convex meniscus forms. Slide a cover glass over the top of the cell, and measure the vertical distance between the bottom of the liquid and the bottom of the cover glass, by means of the fine adjustment scale. The measurement should be made several times, and owing to the possibility of backlash, the fine adjustment screw should turn upward for each reading. For ease in focusing, a tiny smear of thinned drawing ink may be placed on the bottom of the cell chamber and the bottom of the cover glass and then dried, prior to the introduction of the liquid.

The actual depth of the empty cell is measured in exactly the same way. The accuracy of such measurements is about ±0.008 refractive index units under optimum conditions. Since the micrometer fine-adjustment scale may not be uniform, it is advisable to use the same portion each time, i.e., start the readings near either the lower or the upper limit of the movement.

For more accurate measurements, the graphical method is recommended.[2] The apparent depth of the cell is measured for a series of liquids of known refractive index (water 1.333, chloroform 1.446, nitrobenzene 1.553, α-bromonaphthalene 1.658). The values obtained are plotted against the known indices to give a curve that passes through a point $n = 1.0$ (depth = actual depth). This gives a permanent calibration chart from which the refractive index of an unknown liquid may be found from its apparent depth value, with an accuracy of about ±0.003.

FIG. 159.—Jelley-Nichols microrefractometer (schematic presentation of plane of light passing through cell).
Y' = hairline drawn on base of prisms
Z and Z_1 = observed locations of Y'
L = liquid with lower refractive index than that of prisms G and G_1
$N_1 > N_2$, $N > N_2$, $N = N_1$

Unless the liquid has a large temperature coefficient, ordinary temperature changes do not greatly affect the values measured.

An alternative and more accurate method of measuring the refractive index of liquids is that developed by Jelley (see Nichols[21]). The construction of Nichols' microrefractometer is shown in Fig. 159. Two tiny glass prisms are cemented side by side and in opposition on the surface of an ordinary glass slide. A surrounding ring acts as a cell which holds 6 to 100 cu. mm. of liquid. Filtered yellow light enters the cell from below and is refracted from the two prisms as shown. The amount of refraction is noted by observing the apparent separation of the two images of a line Y_1 etched on the slide. The observation is carried out by means of an 80× to 140× microscope equipped with an ocular micrometer, preferably filar. A plot is constructed from data on several liquids of known index, and determinations of unknowns are made graphically to ±0.0005. Alber and Bryant[22] recommend the use of prisms of refractive index 1.52 for

liquids below $n = 1.40$ and above $n = 1.65$, and prisms of refractive index 1.72 for the ranges $n = 1.40 - 1.65$ and $n = 1.85 - 2.0$ (see also Sec. 195).

Sellerio[27] describes still another means of measuring refractive index with the microscope, which is somewhat more precise but which requires accessory equipment consisting of a special ocular and a small lens.

126. Particle Counts.—To count the number of particles in a given volume of liquid, it is necessary to take a minute sample of known volume, spread it over a known area, and count the number of particles in a known portion of this area. Alternatively, an originally unknown volume may be computed from measurement of the depth and area of the containing cell (see below).

Various cells are available for particle counting, which are similar in that they consist of a shallow rectangular or circular depression of uniform known depth which is filled with liquid and covered with a cover glass. The depth of liquid should be as small as possible if fine particles are to be counted. Standard depths vary from 1 to 0.02 mm. Since it would be exceedingly laborious to count particles over the entire area of the cell, it is customary to use a micrometer net ruling on the bottom of the cell and to count particles in several small sections of the area. It is also possible to use an ocular micrometer net or a camera lucida and graph paper to divide the field area into fractions, the only requirement being that each coordinate section be a known fraction of the entire area presented by the cell.

Experimental.—Pipette 0.01 cc. starch solution onto a slide. Cover with a cover glass 1 cm. square so that the total area of the liquid is sharply defined by the edges of the cover glass. Permit the preparation to dry somewhat and, meanwhile, determine the diameter of the field of a 4-mm. objective by means of a stage micrometer. Count the number of starch grains visible in several fields and, knowing the area of each field ($\pi d^2/4$), calculate the number of starch grains per cubic centimeter.

Repeat the preceding particle count, using the drawing ocular. The graph paper may be moved toward or away from the eye point until each square represents a simple fraction of the cell. (The draw tube may be manipulated also.)

Repeat, using an ocular micrometer net, manipulating the draw tube until the squares are of convenient area.

Repeat, using a standard hemocytometer or ruled cell.

127. The Mechanical Stage (Fig. 160).—This is a device that may be clamped on the permanent stage of a microscope so that the microscopist may move a slide back and forth in two directions, by means of two rack-and-pinion movements. Because of the slowness and steadiness with which the slide may be moved, the mechanical stage is exceedingly useful for observations at high magnification. The mechanical stage has a
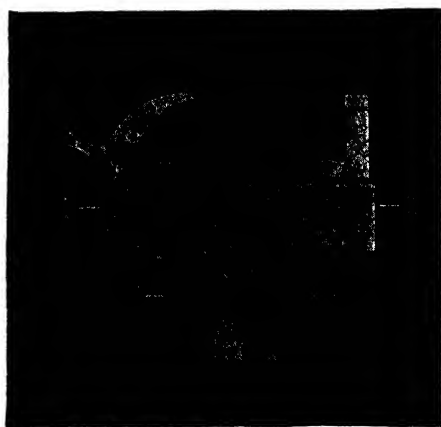
Fig. 160.—Mechanical stage.   (*Courtesy of Bausch & Lomb Optical Company.*)

further advantage in that it may be graduated along two directions so that the "latitude and longitude," or x and y coordinates, of some object on the slide may be recorded on the slide label. When it is desired to locate this particular object, the stage is simply set to the recorded position and the object is located at once.

The mechanical stage is also used when it is necessary to count a series of particles. The procedure is illustrated by the following experiment on fiber analysis.[6]

Experimental.—Boil a 1-in. square piece of paper in 0.5 per cent sodium hydroxide solution for about a minute. Rinse and loosen fibers by rolling the paper in little balls between the fingers. Place a ball of pulp in a small beaker half-full of water, and stir with a motor stirrer to disperse the fibers. Use an

unconstricted pipette 6 mm. in diameter to transfer a small drop of the fiber suspension to a microscope slide. Remove excess water by means of hardened filter paper. Place a drop of Herzberg stain* on the thinly spread pulp, and cover with a cover glass. Examine the slide under the microscope, and note any differences in color between various fibers. Herzberg stain colors fibers as follows:

Wine red or browned pink—rag, cotton, linen, hemp.

Dark blue—jute, bleached straw, chemical wood fibers.

Yellow—unbleached jute or straw, mechanical wood fiber, or fibers high in ligno cellulose.

The various colors having been observed, the quantitative composition of the paper is obtained as follows: Place the slide in the jaw of a mechanical stage. Using a magnification of $100\times$, count the number of red, blue, or yellow fibers along a series of straight lines, twice lengthwise (x) and four times cross-wise (y), by moving the stage along the x or y coordinate and counting each type of fiber as it passes the intersection of the ocular cross hairs. At least 600 fibers should be so counted. For further information on fiber analysis, see "The Microscopic Identification of Paper Fibers," by Whitney and Woodman.[7]

128. The Ultramicroscope.—This may be described as a microscope equipped with an accessory that permits dark-field or lateral illumination of high intensity. There are various accessories for the purpose, ranging from the complicated lateral illuminator[8] and the cardioid dark-field condenser[9] of Siedentopf (Fig. 161) to the relatively simple device of Doane and Dow.[10]

The principle underlying all these ultramicroscopes is the fact that intense lateral illumination causes submicroscopic particles ($0.005\ \mu$ or larger) to become visible, much as dust particles are made visible in a sunbeam or searchlight beam. The actual particles themselves are well below the resolving power of the best lenses, but their diffraction disks may be seen as tiny points of light by even a low-power microscope. Since these diffraction

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* Herzberg stain: Dissolve 50 g. dry zinc chloride (fused) in 25 cc. distilled water. Adjust specific gravity to 1.8 at 28°C., and pour into tall graduate. Rinse hydrometer, etc., with a portion of 12.5 cc. distilled water, and add to zinc chloride solution. In the rest of the 12.5 cc., dissolve 5.25 g. potassium iodide and 0.25 g. iodine. Add to zinc chloride solution, and after 12 hr. standing, decant the clear liquid into a brown bottle. Add a speck of iodine. This stain keeps for several weeks.

disks are in the form of concentric rings, it is obvious that no observations of form are possible, except in the case of irregular particles which do not scatter light equally in all directions.   By indirect means, it is possible to obtain much information from ultramicroscope observations, *e.g.*, size, refractive index, and cataphoretic movement.
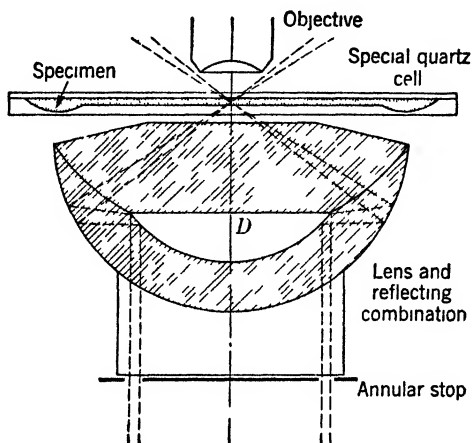
Fig. 161.—The cardioid condenser (simplified).

129. Fluorescence Microscopy.—Certain materials exhibit a characteristically colored fluorescence in ultraviolet light, which permits microscopic identification.   Further, certain substances may be "dyed" with fluorescent substances and then examined microscopically.   The technique requires an intense source of illumination rich in ultraviolet, a filter or filters to isolate the ultraviolet, and a condensing system transparent to ultraviolet light.   Probably the best source is the high-pressure capillary mercury arc which is now commercially available.   An alternative source is the d.c. iron arc or nickel-graphite arc, although some workers use a high-voltage spark discharge, which, however, has the disadvantage of noise and expense of equipment.

Filters are made especially for isolation of the ultraviolet region (4,000 to 3,000 A or lower).   Wood's glass, with a nickel oxide base, is frequently used, and also Corning glass 587 or 597.   A thin quartz or Corex cell containing a solution of nitroso-dimethyl-aniline, with a thicker cell containing dilute copper sulfate, may be used, either with or without a uviol glass or ultra glass filter.

For further information on filters, see Gray,[15] Miethe and Stengel,[16] Bowen,[17] Vaidja,[18] and Doetsch.[19]

The illuminating system of the microscope consists of a quartz reflecting prism or an aluminized mirror, which replaces the usual mirror, and a quartz dark-field condenser. The slides used must be of quartz or some ultraviolet transparent material such as uviol glass. Glycerin is commonly used as an immersion medium because the conventional oils exhibit fluorescence. Menthol has been recommended as a mounting medium. The cover glass need not be transparent to ultraviolet, but it should not fluoresce.

130. The Hot Stage.—An electrically heated microscope stage, which may be temporarily mounted in place of the regular revolving stage, is of great use to the organic chemist for observation of melting point, critical solution temperature, etc. The melting of *individual* crystals in a mixture may be observed. The hot stage and also the cold stage are useful for studies of allotropy and phase equilibria. Chamot and Mason[2] give several designs for such stages, and ready-made equipment is available, although the construction is so simple that anyone with access to a lathe may build his own device.

The use of the polarizing microscope in conjunction with the hot stage for determining melting points greatly increases the accuracy of measurement ($\pm 0.1°C.$), because the intense and easily observable polarization colors (Sec. 170) disappear instantly when an anisotropic crystalline substance melts.

131. *The utility of the microscope in qualitative analysis* places it foremost in the list of indispensable optical instruments. There is scarcely a single branch of analytical chemistry where an important application of the microscope has not been found. Several schemes have been devised whereby ordinary qualitative reactions are carried out in drops on a microscope slide,[2] and not only is the sensitivity of these reactions multiplied a hundredfold, but also it is actually possible in many instances to carry out an analysis more rapidly by micro-methods than by test-tube methods. The saving in time is due principally to elimination of lengthy filtrations and digestions and the time-consuming process of preparing the sample for analysis. Alkali fusions, for example, take only a moment when conducted by the soda-bead technique.

Often the simple microscopic observation of a sample will reveal its structure and content, *e.g.*, an etched-steel surface, a

finely powdered mixture of pigments, or a mixture of crystals of different types.   The general statement may be made that the chemical analysis of any heterogenous sample should be preceded by a thorough microscopic examination.   The information so obtained may save a great many hours of chemical analysis. Particle counts may be particularly useful for discrete mixtures, since rough quantitative results are obtained directly.

Instead of listing and describing the manifold applications of chemical microscopy, the student is referred to two excellent reviews: the reports of a symposium held in 1920 by four British societies,[25] and the recent review by Griffiths *et al.*[26]   It is interesting to compare these two publications, since the first gives the historical development of the microscope, its uses prior to 1920, and many suggested uses that have subsequently been developed and reported in the more recent survey.   Both references include extensive bibliographies.   (A number of important applications are referred to in Prob. 8.)

SUPPLEMENTARY NOTES ON EQUIPMENT

132. *For the educational laboratory* (four students):

4 microscopes with rotating stage, substage condenser and diaphragm, and the following accessories:

   10× ocular.
   16-mm. and 4-mm. objectives.
   Nosepiece.
   Focusable condenser, with diaphragm and dark-field stops.
1 oil-immersion objective and condenser.
1 vertical illuminator and special lamp.
4 lamps of chalet or similar type.
2 positive ocular micrometers (0.1-mm. divisions).
2 stage micrometers (0.1- and 0.01-mm. divisions).
2 camera lucidas.
2 counting cells (Sedgwick-Rafter) or hemocytometers.
2 cells for refractive index determination.
1 mechanical stage.
1 cardioid condenser and accessories.
1 spinning table and enamel.
2 sets of chemicals as follows:
   Immersion liquids.
   Mounting media.
   Cleaning solutions.
   Titanox or other white paint pigment.

Herzberg stain.

Powdered glass.

Starch solution (preserved with chloroform).

2 sets of slides as follows:

Starch in Canada balsam.

Microscopic silver beads (for measurements).

Section of a lamp filament (for measurements).

Diatoms, especially *Amphipleura pellucida*.

Various paper and textile fibers.

Objects of interest as selected by the instructor, *e.g.*, bacteria (stained and mounted), butterfly wing, feather, or other biological specimens. (An infusion of hay kept a few days in a large glass flask stoppered with cotton wool furnishes interesting material.)

PROBLEMS

1. Sketch the mechanical system of a compound polarizing microscope from memory, naming all the parts.

2. Sketch the optical system of the compound microscope, naming each part, and giving the functions of all lenses and diaphragms.

3. What is the resolving power for parallel rays and for convergent illumination of an objective whose N.A. = 1.0? If the full aperture of the objective is not filled with light, what is the effect on the resolving power?

4. If the highest possible angular aperture of an objective is 180°, what is the maximum resolution attainable in air? In cedaro il? (Assume wave length of 5,600 A.)

5. A microscope and illuminating system are adjusted according to custom, and a finely divided specimen is examined. State the observed effects of (*a*) stopping down the condenser; (*b*) opening the condenser to its maximum aperture; (*c*) lowering the condenser; (*d*) raising the condenser as far as possible; (*e*) raising the draw tube and refocusing.

6. Would it be feasible to substitute a negative ocular micrometer in the experimental determination of magnification described in Sec. 99? Give reasons.

7. If the resolving power of an objective is 0.00001 in. at 5,600 A (converging light), estimate the resolving power at 2,536 A. Use of the equation

$$R = \frac{2 \text{ N.A.}}{0.6\lambda}$$

results in a somewhat more accurate value for the ultraviolet region.

8. Write a two- or three-page survey illustrating the versatility of the microscope, including material in this chapter and in some of the following references:

"The Polarizing Microscope As a Polarimeter," by A. Marion, *Ind. Eng. Chem. Anal. Ed.*, **12**, 777 (1940).

"A Microphotometer for Spectrochemical Analysis," by E. M. Thorndike, *Ind. Eng. Chem. Anal. Ed.*, **13**, 66 (1941).

"Quantitative Analysis by Particle Counting" in Vol. I, "Handbook of Chemical Microscopy," by Chamot and Mason, John Wiley & Sons, Inc., New York, 1938.

"Microchemical Analysis" in Vol. II, "Handbook of Chemical Microscopy," by Chamot and Mason.

"The Limits of Simple Confirmatory Tests," by Benedetti-Pichler and Rachele, *Ind. Eng. Chem. Anal. Ed.*, **12**, 229 (1940).

"The Microspectroscope," in Vol. I, "Handbook of Chemical Microscopy," by Chamot and Mason.

"The Microscope As a Colorimeter," in Vol. I, "Handbook of Chemical Microscopy," by Chamot and Mason.

"Textile, Wood, Paper and Starch Analysis," in "Industrial Microscopy," by L. C. Lindsley, Byrd, 1929.

Also include such topics as criminological, pharmaceutical, and biological uses, as well as utility in colloid chemistry, food analysis, mineralogy, metallography, toxicology, etc.[25,26]

REFERENCES

1. C. Beck, "The Microscope," R. and J. Beck, London, 1938.
2. E. M. Chamot and C. W. Mason, "Handbook of Chemical Microscopy," John Wiley & Sons Inc., New York, 1938.
3. S. H. Gage, "The Microscope, Dark-field Edition," Comstock Publishing Company, Inc., Ithaca, N. Y., 1936.
4. H. Landolt, *Ber.*, **27**, 2872 (1894). See also reference 5.
5. N. W. Hartshorne and A. Stuart, "Crystals and the Polarizing Microscope," Edward Arnold & Co., London, 1934.
6. T. M. Plitt, *Bur. Standards Circ.*, C423, 1939.
7. W. R. Whitney and A. G. Woodman, "Microscopic Identification of Paper Fibers," *Technology Quarterly*, Vol. 15, No. 3 (1902).
8. H. Siedentopf, *Z. wiss. Mikrosk.*, **26**, 391 (1909).
9. H. Siedentopf, *Verb. deut. physik. ges.*, **12**, 6 (1910).
10. H. C. Doane and W. A. Dow, *J. Chem. Education*, **6**, 1099 (1929).
11. M. Haitinger, "Die Fluoreszenzanalyse in der Mikrochemie," E. Haim, Vienna, 1937.
12. J. A. Radley and J. Grant, "Fluorescence Analysis in Ultra-violet Light," Chapman & Hall, Ltd., London, 1937.
13. T. H. Daugherty and E. V. Hjort, *Ind. Eng. Chem. Anal. Ed.*, **6**, 370 (1934).
14. E. A. Hauser and C. J. Frosch, *ibid.*, **8**, 423 (1936).
15. L. T. M. Gray, *J. Phys. Chem.*, **51**, 1732 (1927).
16. A. Miethe and E. Stenger, *Z. wiss, Phot.*, **19**, 58 (1919).
17. E. J. Bowen, *J. Chem. Soc.*, **76** (1935).
18. B. K. Vaidja, *J. Univ. Bombay*, **3**, 141 (1934).
19. J. Doetsch, *Anales Fis. quim.*, **35**, 65 (1934).
20. F. E. Wright, *J. Wash. Acad. Sci.*, **4**, 269 (1914).
21. L. Nichols, *Nat. Paint Bull.*, **1**, 12 (1937).

22. H. K. Alber and J. T. Bryant, *Ind. Eng. Chem. Anal. Ed.*, **12, 305** (1940).

23. L. C. Graton and E. B. Dane, *J. Optical Soc. Am.*, **27,** 355 (1937).

24. L. C. Martin and B. K. Johnson, *J. Sci. Instruments*, **2,** 337 (1928); **7,** 1 (1930).

25. F. S. Spiers, "The Microscope," Charles Griffin & Company, Ltd., London, 1920.

26. J. G. A. Griffiths, G. C. Gull, and H. K. Whalley, *Ann. Repts. Chem. Soc.*, **36,** 389 (1940).

27. A. Sellerio, *Nuovo cimento*, **3,** 190 (1926).

CHAPTER V

ELEMENTARY CRYSTALLOGRAPHY

133. A working knowledge of geometrical crystallography is a necessary prerequisite to the study of optical crystallography, X-ray diffraction, and chemical microscopy. Because of its fundamental nature and practical importance, crystallography is likewise useful in practically all phases of chemistry. The mere outline presented here is intended only as an introduction which will enable the student to read more advanced texts intelligently.[1,2,3,4,7,9,10,13]

134. Fundamental Definitions and Laws.—The former definition of a crystal as a "solid bounded by naturally plane surfaces" has been radically modified by more or less recent theoretical* studies. The modern concept of crystallinity involves an arrangement of constituent atoms, ions, or molecules in definite and regular, interpenetrating, three-dimensional patterns or point systems. Since this definition includes certain solids usually considered amorphous, and also certain liquids, it is perhaps advisable to postulate a compromise definition or working description for the purposes at hand, *viz.*, a crystal is a solid naturally bounded by plane surfaces, whose atoms, ions, or molecules are arranged in a definite regular pattern.

When a crystal is formed under ideal conditions, its various faces develop symmetrically, following the planes of the atomic lattice, to form a geometrical solid such as a cube or rhombohedron. These ideal forms are not always encountered in practice, for conditions of growth may inhibit some faces while exaggerating others to such an extent that the crystal becomes unrecognizable. In such a case, it is necessary to disregard the superficial appearance and to consider the implication of the second part of the "working definition" in the form of a rule: development of a crystal face parallel to its original position does not affect the symmetry of the crystal. Since the arrangement of the atoms remains intact, irrespective of the outward form, it is obvious that this internal structure must form the basis

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for crystallographic study.   The fundamental law which permits deduction of ideal geometrical forms from observations of distorted crystals is that the various plane surfaces of a crystal are parallel to planes of atoms within the crystal.   This is illustrated in Fig. 162, where the dots represent atoms arranged in a crystal lattice, and the shaded areas are typical planes of atoms that may develop into crystal faces.   All the possible atomic planes need not form faces, but those faces which are formed as the crystal grows *are* parallel to atomic planes.   The combination of planes selected by the crystal is called the *habit* of the crystal.
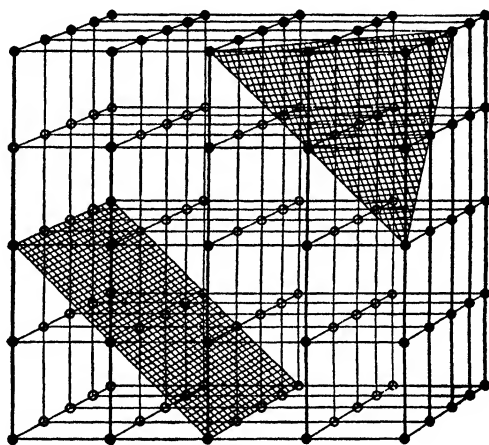
Fig. 162.

Since the atomic planes are never distorted, it follows that *in all crystals* of a given *substance the angles between corresponding faces are constant.*   This law holds true no matter what the size or shape of the face may be.

Consideration of the geometry of the situation shows that by measuring the angles between the various faces of the crystal, no matter how large or small or poorly defined these faces are, it is possible to reconstruct the ideal form of the crystal with considerable accuracy.

135. Measurement of Crystal Angles.—The instrument usually used for the measurement of crystal angles is called a reflecting goniometer, the principle of which is illustrated in Fig. 163.   The crystal to be studied is mounted, by means of some wax, on a rod which is the axis of a rotating circular scale.

The rotating scale is then turned until the image of a distant light source is reflected from some face of the crystal. The scale is read, and the drum is rotated until the image reflected by an adjoining face is seen. The angular differences between the two readings is the supplement of the angle between the two faces.

A two-circle goniometer is used for refined work. It has two axes of rotation with corresponding graduated scales and permits complete study of a crystal, *i.e.*, location of faces, measurement of angles, and calculation of axial intercepts, from a few settings of the crystal. Crystals as small as 0.5 mm. may be studied by
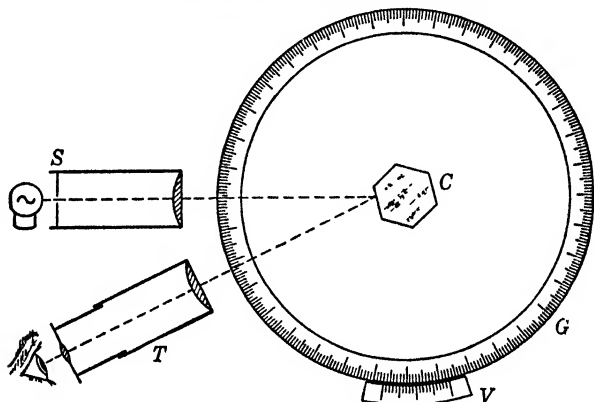
FIG. 163.—Goniometer (spectrometer type). Crystal *C* is fixed to shaft of graduated circle *G*. The image of illuminated slit or mark *S* is reflected from a face of the crystal and observed through telescope *T*. The scale reading of vernier *V* is noted, and the circle is turned until another face reflects the image of the slit. The angle through which the circle has been turned is the angle between normals to the two faces and equals the supplement of the angle between the faces.

means of such instruments, and measurements are frequently reported to 0.001°.

Chemical compounds that may be obtained in the form of well-developed crystals of suitable size may be identified by precise measurement of the interfacial angles. The crystallographic constants of many compounds have been tabulated by Groth[9] and Winchell.[13] The classification system of Barker[10] is much more convenient, from the point of view of the analyst, however.

It is possible to measure silhouette angles of crystals that are formed on a microscope slide, by means of the rotating stage. The crystal is placed so that the intersection of two edges is at the center of the ocular cross hairs. One edge is aligned with a

cross hair, the stage reading is noted, and the stage is rotated until the other edge is aligned with the cross hair. At least 10 readings should be made to obtain significant accuracy, and the result must be checked with several other crystals.[11]

SYMMETRY

136. Consider now the ideal, undistorted crystalline solid, where the outward appearance is completely governed by the
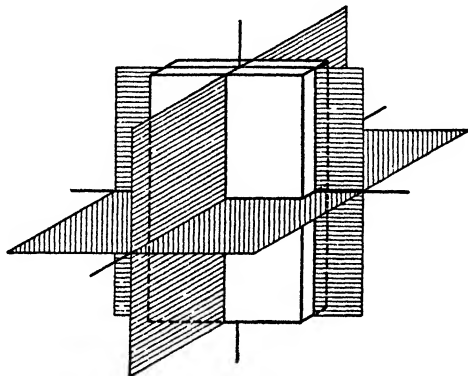
Fig. 164.

regular internal arrangement of atoms. It follows that, owing to the very regularity of the atomic lattice, the outward appearance of the crystal must also exhibit a degree of regularity or symmetry. This symmetry may be about a plane, a line, or a point, and since it is the expression of the internal structure, it follows that all crystals of the same substance have the same grade of symmetry, polymorphs excepted.

137. Symmetry about a Plane.—If an ideal crystal may be cut in two along some plane and one-half placed against a mirror in such a way that the reflected image seems to replace the

Fig. 165.—Top view.

missing half, then the crystal is symmetrical about that plane. In other words, a crystal is symmetrical to a plane if for each face, edge, or angle on one side of the plane there is a similar face, edge, or angle exactly opposite on the other side of the plane. Nonideal crystals do not accord with this definition
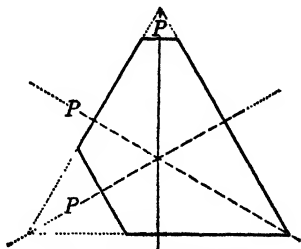
because certain faces, needed to complete the symmetry of a given face, may not have developed. Thus a more general definition of a plane of symmetry is that it has on opposite sides a similar distribution of similar points. Figure 164 shows a crystal with planes of symmetry. Note that the angular
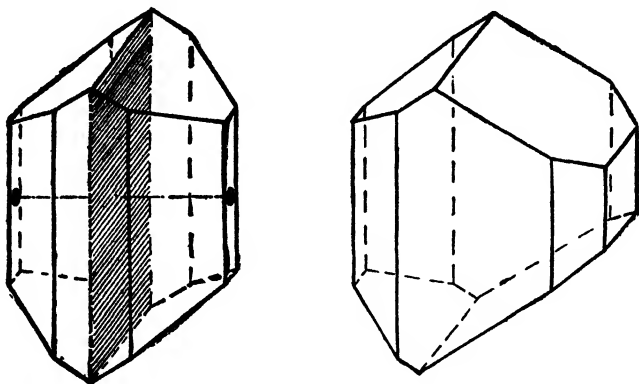
FIG. 166.

position of the faces is the determining factor of symmetry and not the size or distance between faces (Figs. 165 and 166). The symbol indicating a plane of symmetry is the capital letter P.

138. Symmetry about a Line.—If a crystal may be revolved
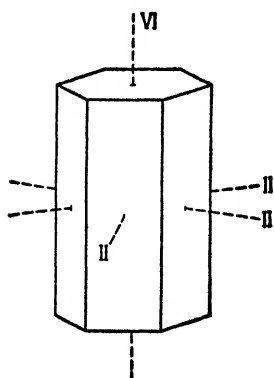
FIG. 167.

about some axis so that each face or group of faces is replaced by a similar face or group of faces n times during a complete revolution, then the crystal has a line or axis of n-fold symmetry. Only axes of two-, three-, four-, and sixfold symmetry are found. These are designated by A_2, A_3, A_4, and A_6 preceded by an arabic numeral indicating the number of axes of n-fold symmetry present. Figure 167 shows a crystal having an axis of sixfold symmetry and several axes of twofold symmetry. A special type of symmetry involves reflection across a plane and then rotation about an axis. The plane of reflection is called a *plane of compound symmetry* (*cP*) and the axis is an *axis of alternating symmetry* (*cA*) (see Fig. 168).

139. Symmetry about a Point.—Many crystals have a *center of symmetry*. This center is a point such that all straight lines that can be drawn through it pass through two identical points located on opposite sides of the center. Thus, for each face of the crystal, there is a corresponding face on the opposite side
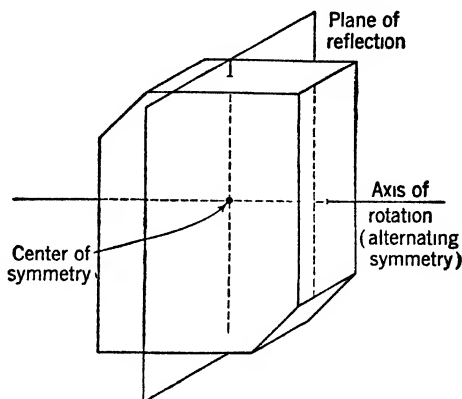
FIG. 168.

of the center of symmetry (see Fig. 168). If a perfect crystal is laid on a table top so as to rest on some particular face, a corresponding face will be uppermost if there is a center of symmetry. Further, if a crystal has a center of symmetry, there will be an axis of symmetry at right angles to every plane of symmetry, and vice versa. The symbol used to indicate the presence of a center of symmetry is the small letter *c*. (The center of symmetry is a special case of compound symmetry, since it is equivalent to reflection across a plane and rotation of 180° about an axis, as shown in Fig. 168.)

FIG. 169.

140. Crystallographic axes are geometric coordinate axes that permit definition of crystal faces in terms of simple intercepts. Conventionally, and for the sake of convenience, the axes are chosen so that they are parallel to the principal edges of an ideal crystal. Thus, to describe a cubic crystal, three mutually perpendicular equal axes are chosen; and to simplify the description of a triclinic crystal, whose planes can-

not be described by integral intercepts on perpendicular axes, a set of oblique coordinate axes is chosen (Figs. 200 and 201).
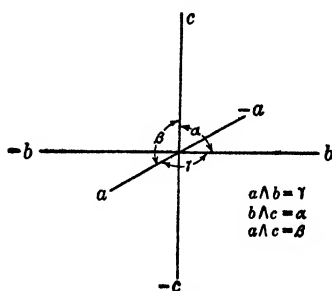
Whatever the relation between axes, they are oriented and designated as in Fig. 169, the positive end of the a axis toward the observer, the b axis pointing to this right hand, and the c axis vertical. The angles between the axes are designated by α, β, and γ as shown.
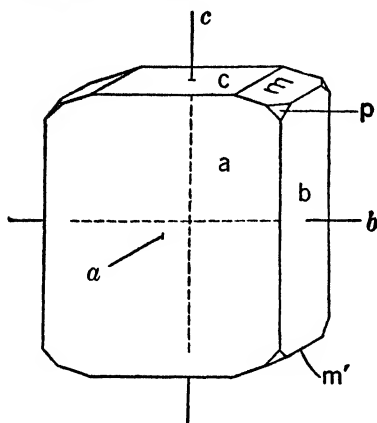
FIG. 170.

141. Miller Indices.—As mentioned above, a crystal face may be designated in terms of its intercepts on three axes, provided that it is possible to orient the crystal properly with respect to the axes (see following pages). The intercepts of a face on three axes may be very accurately measured by means of the goniometer (Sec. 135) or less accurately by various other methods.

Consider the orthorhombic crystal shown in Fig. 170: let the intercepts of faces a, b, m, p, and c on axes a, b, and c be as follows:

Face	Measured intercepts		
	a	b	c
p	2.08	2.24	3.88
a	1.04	∞	∞
b	∞	1.12	∞
m	∞	3.36	1.94
c	∞	∞	0.97

Any one of these four faces may thus be defined in terms of the measured intercepts on three axes, but such a notation would be cumbersome. A method of simplifying the designation of faces has been developed by W. H. Miller. According to the Miller system, a face is expressed in terms of the three quotients

$$\frac{a \text{ parameter}}{a \text{ intercept}}; \quad \frac{b \text{ parameter}}{b \text{ intercept}}; \quad \frac{c \text{ parameter}}{c \text{ intercept}}$$

where the *parameter* for any axis is the relative length of the intercept, on that axis, of some one selected face designated as the *parametral face*. The parametral face selected is usually a face which if extended cuts all three axes, *i.e.*, a pyramid face, and although the selection is more or less arbitrary, it is not critical.

If face *p* (Fig. 170) is selected as the parametral face, the relative lengths of the three intercepts are 2.08, 2.24, and 3.88 for the *a*, *b*, and *c* axes, respectively. These relative values are usually simplified so that the *b* parameter equals unity. Thus, 2.08 : 2.24 : 3.88 : :0.93 : 1 : 1.73. The values of 0.93, 1, and 1.73 are then the parameters. The ratios *a/b* and *c/b* which are used in crystallographic descriptions are called the *axial ratios*. In order to simplify this discussion, the relative values of all the intercepts are reduced in the same ratio.

Face	Reduced intercepts		
	a	*b*	*c*
p	0.93	1	1.73
a	0.465	∞	∞
b	∞	0.5	∞
m	∞	1.50	0.866
c	∞	∞	0.433

To obtain the Miller indices of the various faces, the parameters are divided by the relative values of the intercepts, as follows:
Face *p*:

$$\frac{0.93}{0.93}; \quad \frac{1}{1}; \quad \frac{1.73}{1.73} = 1; \quad 1; \quad 1 = \text{Miller index which is written 111.}$$

Face *a*:

$$\frac{0.93}{0.465}; \quad \frac{1}{\infty}; \quad \frac{1.73}{\infty} = 200$$

Since all parallel faces are equivalent (see Sec. 134), it is immaterial whether this face is designated as 200, 300, or 100. In practice only, the latter index is employed. The Miller index of face *a* is thus 100.
Face *b*:

$$\frac{0.93}{\infty}; \quad \frac{1}{0.5}; \quad \frac{1.73}{\infty} = 0; \quad 2; \quad 0 = 010$$

Face m:

$$\frac{0.93}{\infty}; \quad \frac{1}{1.50}; \quad \frac{1.73}{0.866} = 0; \quad \tfrac{2}{3}; \quad 2 = 013$$

Note that these are the smallest possible whole numbers that can designate this face and that the rule cited above for face a still holds.

Face c:

$$\frac{0.93}{\infty}; \quad \frac{1}{\infty}; \quad \frac{1.73}{0.433} = 0; \quad 0; \quad 4 = 001$$

Face m':

$$\frac{0.93}{\infty}; \quad \frac{1}{1.50}; \quad \frac{1.73}{-0.866} = 0; \quad \tfrac{2}{3}; \quad -2 = 01\bar{3}$$

From the foregoing, it is apparent that for any face q if a, b, and c are the parameters, x, y, and z the intercepts on the three axes, and h, k, and l the Miller indices, then

$$\frac{a}{x} : \frac{b}{y} : \frac{c}{z} = h : k : l$$

One consequence of the regularity of crystal structure is the law of rational indices, which states that the indices h, k, and l may be expressed as whole numbers or zero.

Several factors must be borne in mind regarding the use of the Miller system:

1. When the intercept of any face such as m' (Fig. 170) is negative, the corresponding index is negative. (The indices of face m' are read as "zero, one, bar three.")

2. The larger the intercept of any face on an axis, the smaller the Miller index for that axis.

3. Any face that bevels the intersection of two faces so as to make approximately equal angles with each is said to truncate the edge of the two faces. [Face (101) truncates the edge of faces ($1\bar{1}1$) and (111) in Fig. 172.] The indices of such a face may be found by adding the indices of the truncated faces. ($1\bar{1}1$) + (111) = (101). If the beveling face does not make equal angles with the two faces, this relation does not hold.

4. The symmetry of a crystal usually requires the presence of several identical faces to complete the symmetry of a given face. In Fig. 171, the face (111) requires the presence of seven other faces to complete its symmetry. The total faces (111, $1\bar{1}1$, $\bar{1}\bar{1}1$, $\bar{1}11$, $11\bar{1}$, $1\bar{1}\bar{1}$, $\bar{1}\bar{1}\bar{1}$, $\bar{1}1\bar{1}$)

constitute a *form*.   An abbreviation for the form is simply the enclosure of any face belonging to the form in braces, thus: {111}.

142. Naming of Faces; Use of Terms and Symbols.—Crystal faces are best designated by the Miller system, but it is often convenient to name a face or form according to the following definitions:

Pinacoid.   A face or form parallel to two axes and cutting the third. A *basal pinacoid* cuts the *c* axis (faces *a*, *b*, *c*, Fig. 170).

Prism.   A face or form parallel to a vertical axis and cutting the other two (face 110, Fig. 172).

Dome.   A face or form parallel to a horizontal axis and cutting the other two (face 101, Fig. 172).

Pyramid.   A face or form which if extended cuts all three axes (Fig. 171).
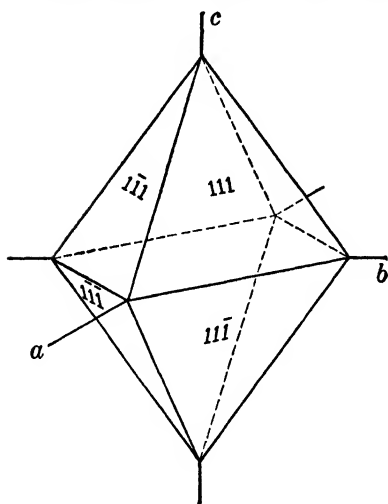
FIG. 171.
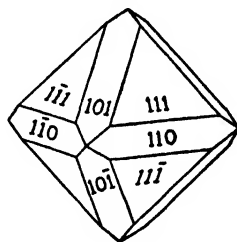
FIG. 172.

Bipyramid.   A complete form of pyramids.   Two geometric pyramids placed base to base (Fig. 171).

Sphenoid.   Two faces whose intersection is parallel to a twofold axis (Fig. 181).

Zone.   A series of faces with parallel intersections.   (Faces may be extended if necessary.)

Hemi-.   Prefix used with prism, dome, etc., indicating that only half of the complete form is present.

Holohedrism.   Development of all faces of a form.

Hemihedrism.   Development of half the faces of a form.

Tetartohedrism.   Development of one-quarter the faces of a form.

Hemimorphism.   Crystals that are differently terminated on opposite ends of an axis of symmetry which is also a crystallographic axis (*e.g.*, tartaric acid crystals that exist in two forms, one the mirror image of the other).   Such crystals are also called uniterminal (Fig. 192).

THE SEVEN CRYSTAL SYSTEMS

143. The classification of all crystals into seven *systems*, or symmetry groups, is a logical consequence of the nature of the atomic or space lattice.   Reasoning from purely mathematical considerations and a theory of the space lattice, Bravais, Sohnke, and others (1848 to 1894) showed that there can be 230 possible arrangements of atoms in a crystal, such that each equivalent atom has the same grouping of surrounding atoms.   These 230 possible arrangements possess only 32 types of symmetry, corresponding to the 32 *classes* of crystals, and the symmetry of these 32 classes may be further divided into seven main divisions corresponding to the seven crystal *systems*.   The fundamental sym-

TABLE 13.—THE SEVEN CRYSTAL SYSTEMS

Symmetry	Axes of reference	System
More than one axis of three- or fourfold symmetry	Three equal axes mutually perpendicular	Isometric (cubic) (Fig. 174)
Only one axis of sixfold symmetry (hexagonal axis)	Three equal axes making angles of 60° (120°) in one plane, and one un-equal axis normal to that plane	Hexagonal (Fig. 178)
Only one axis of threefold symmetry (trigonal axis)		Rhombohedral (trigonal) Fig. 181)
Only one axis of fourfold symmetry (tetragonal axis)	Three mutually perpendicular axes, two of equal length, one unequal	Tetragonal (Fig. 185)
Two or more axes of twofold symmetry or one axis of twofold symmetry and two planes of symmetry	Three unequal axes, all mutually perpendicular	Orthorhombic (Fig. 190)
Only one axis of twofold symmetry or one plane of symmetry or both	Three unequal axes, one normal to the other two which are oblique	Monoclinic (Fig. 195)
Neither axes nor planes of symmetry, may or may not have center of symmetry	Three unequal axes, all oblique	Triclinic (Fig. 201)

metry of a crystal places it in one of the seven systems, whereas the grade or degree of symmetry exhibited assigns it further to a class of that system.

By partial determination of the fundamental symmetry, it is possible to determine the system to which a given crystal belongs, as illustrated by Table 13, which also gives the geometrical axes to which the crystal is most easily referred.

The treatment of the seven systems given in the following sections involves description of the various classes or subgroups of each system.   These classes are described primarily for purposes of reference, since the chemist rarely identifies them.   In studying these sections it is recommended that the student pay particular attention to the illustrations and to the classes which they represent.

144. The Isometric System (Cubic, regular; Tesseral; Tetratrigonal).

Symmetry.—More than one axis of three-or-four-fold symmetry.

Crystallographic Axes.—Three equal, mutually perpendicular axes (Fig. 173) $a = b = c$; $\alpha = \beta = \gamma = 90°$.

Classes.—There are five classes in the cubic system:

FIG.   173.—Crystallographic axes.

Class 32* $4A_3$, $3A_4$, $6A_2$,   9P
  Hexoctahedral.   (Holohedral or normal.)   (Figs. 174 and 175.)
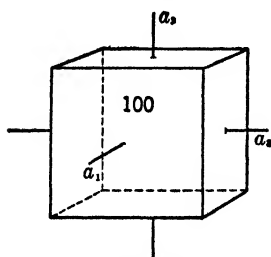
Cube (Class 32)
FIG. 174.
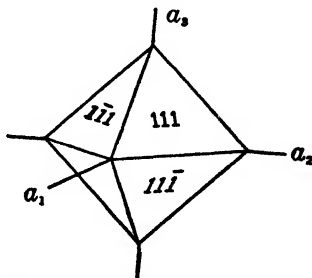
FIG. 175.—Octahedron (Class 32).

* The symbols may be read as follows: Four axes of threefold symmetry, three axes of fourfold symmetry, six axes of twofold symmetry, and nine planes of symmetry.

Class 31 $4A_3$, $3A_2$, 6P Hexatetrahedral. (Tetrahedral.)
(Fig. 176.)
Class 30 $4A_3$, $3A_2$, 3P Dyakisdodecahedral. (Diploidal,
pyritohedral.)
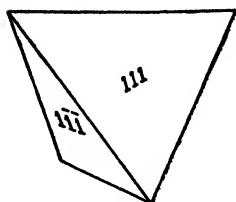
FIG. 176.—Tetrahedron
(Class 31).

Class 29 $4A_3$, $3A_4$, $6A_2$ Pentagonal-ico-
sitetrahedral. (G y r o i d a l, plagiohe-
dral.)
Class 28 $4A_3$, $3A_2$ Tetragonal-pentag-
o n a l-d o d e c a h e d r a l. (Tetartoidal,
tetartohedral.)

(NOTE: A geometrical cube may show
unsymmetrical markings or solvent-induced
"etch figures" indicating a lower grade of symmetry.)

Microscopic Views.—When crystallized on a microscope slide,
crystals of this system are usually very regular or equidimen-
sional. The silhouette views may be square, triangular (as in
views of octahedron and tetrahedron), or triangular with squared
corners. Interfacial angles are of no diagnostic value except
in so far as they aid in identifying the system.

145. The Hexagonal System, Hexagonal Division.

Symmetry.—One axis of sixfold symmetry.

Crystallographic Axes.—Three equal in-
terchangeable axes making angles of 120°
(60°) in one plane and one unequal axis
normal to the plane (Fig. 177). The
axes are always oriented as shown in
Fig. 177, with the unequal c axis vertical.
The apparently anomalous method of
designating the three equal axes is due
to the fact that with the negative (un-
lettered) end of the a_3 axis as shown, all
faces in a form have the same Miller
units, and incidentally, the sum of the
four indices of any face parallel to the c axis is zero. The Miller
indices are given in the order a_1, a_2, a_3, c.

FIG. 177.

$a_1 \wedge a_2 \wedge a_3 = 120°$
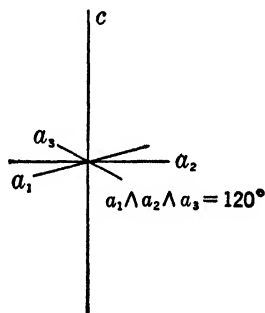
Classes.

Class 27 $1A_6$, $6A_2$, 7P Dihexagonal-bipyramidal. (Holo-
hedral, or normal.) (Fig. 178.)

Class 26 $1A_6$, 6P Dihexagonal-pyramidal. (Hemihedral-dihexagonal.)

Class 25 $1A_6$, normal to P   Bipyramidal or tripyramidal.

Class 24 $1A_6$, normal to $6A_2$ Trapezohedral.

Class 23 $1A_6$ only   Pyramidal. (Hemimorphic pyramidal.)

The terms *first-order* and *second-order* applied to prisms or pyramids refer to the equality or nonequality of the integral intercepts. Thus, $\{10\bar{1}1\}$ is a first-order pyramid, whereas $\{11\bar{2}1\}$ is of the second order.

Microscopic Views.—Hexagonal crystals usually appear in the form of hexagons or polygons, having interfacial angles of 120 or 150°. Occasionally, such crystals appear to be equilateral triangles or triangles with slightly beveled corners. The interfacial angles in the zone parallel to the sixfold axis are not characteristic of the substance.
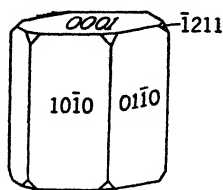
(Class 27)

FIG. 178.

146. The Rhombohedral-hexagonal System (Trigonal, "Rhombohedral Division of the Hexagonal System").

Symmetry.—One axis of threefold symmetry, and only one.

Crystallographic Axes.—Same as for the hexagonal system (Figs. 177 and 179).
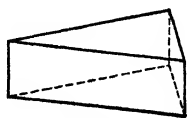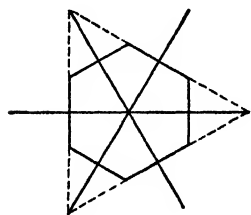
Classes.

Class 22 $1A_3$ normal to P, $3A_2$, 4P Ditrigonal-bipyramidal. (Tetartohedral.)

Class 21 $1A_3$ normal to $3A_2$, 3P Ditrigonal-scalenohedral. (Rhombohedral-scalenohedral.) (Figs. 180, 181, 182.)

Class 20 $1A_3$ and 3P Ditrigonal-pyramidal. (Rhombohedral-hemimorphic.)

FIG. 179.

Class 19 $1A_3$ normal to P   Bipyramidal. (Tetartohedral-hemimorphic.)

Class 18 $1A_3$ normal to $3A_2$ Trapezohedral. (Rhombohedral-trapezohedral.)

Class 17 $1A_3$, cA_6 (compound)   Rhombohedral.

Class 16   1A$_3$ only, no center   Pyramidal.   (Tetartohedral-hemimorphic.)

2$1\bar{3}$1
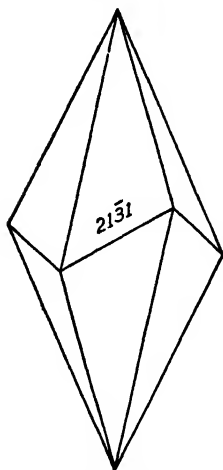
Fig.   180.—Scalenohedron.

10$\bar{1}$1

a_3

a_1

a_2

01$\bar{1}$1
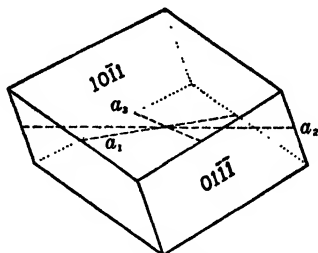
FIG. 181.—Rhombohedron.
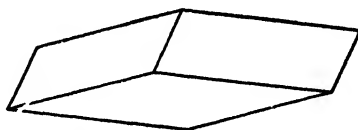
FIG. 182.—An obtuse rhombohedron.

Microscopic Views.—Crystals grown on a microscope slide usually appear in silhouette as rhombs or parallelograms.   Views along the axis of threefold symmetry are rare.

147. The Tetragonal System (Quadratic, Pyramidal). *Symmetry.*—Only one axis of fourfold symmetry.

c

a_2

a_1

$a_1 = a_2 \neq c$

FIG. 183.

c

a_2

a_1
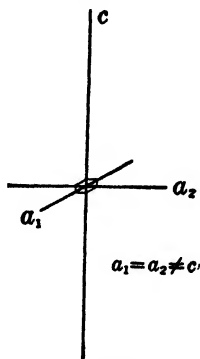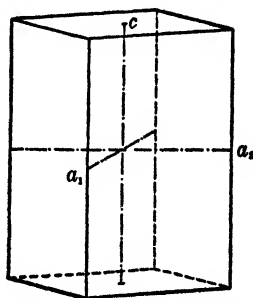
FIG. 184.—First-order prisms (or pinacoids).

Crystallographic Axes.—Three mutually perpendicular axes, two of equal length, one of unequal length.   The three axes are always oriented as shown in Fig. 183.   The unequal axis is

always the *c* axis and is placed vertically. The two equal axes are interchangeable. $a = b \neq c$; $\alpha = \beta = \gamma = 90°$.

Classes.

Class 15 $1A_4$ normal to P; $4A_2$, 5P   Ditetragonal bipyramidal. (Holohedral or normal.)   (Figs. 184, 185, 186, 187.)
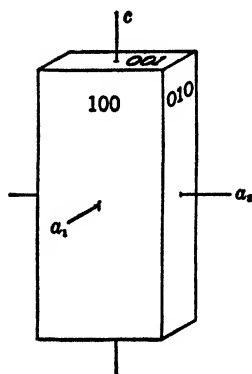
FIG. 185.—Second-order prisms (or pinacoids).
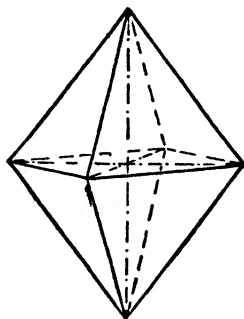
FIG. 186.
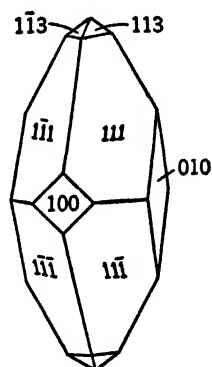
FIG. 187.

Class 14 $1A_4$ normal to cP, $2A_2$, 2P   Scalenohedral. (Sphenoidal.)   (Fig. 188.)

Class 13 $1A_4$ and 4P   Ditetragonal-pyramidal, tetragonal hemimorphic.

Class 12 $1A_4$ normal to P   Bipyramidal or tripyramidal.

Class 11 $1A_4$ normal to $4A_2$ Trapezohedral.

Class 10 $1A_4$ (*c*) normal to cP   Bisphenoidal or tetartohedral.

Class 9 $1A_4$ Pyramidal. (Pyramidal-hemimorphic.)

In this system, the first-order prisms, shown in Fig. 184, may be modified to give second-order prisms, as in Fig. 185, which are also pinacoids. In this connection, the reason for the nonexistence of an axis of eightfold symmetry is apparent from the fact that the zone of prism faces {210} and {120} gives an eight-sided silhouette, which, however, shows an axis of only four-fold symmetry, since the interfacial angles are not all equal.
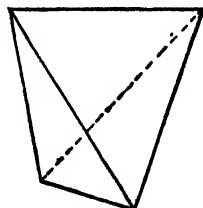
FIG. 188.

Microscopic Views.—Tetragonal crystals generally appear as needles, elongated along the *c* axis, or, more rarely, as slightly

elongated or stunted octahedra.   The appearance of square or rectangular silhouettes is common; these may or may not have beveled corners.

148. The   Orthorhombic   System   (Rhombic,   Prismatic, Trimetric).
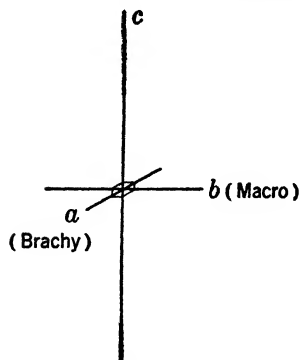
Fig. 189.

Symmetry.—Two or more axes of twofold symmetry, or one axis of twofold symmetry and two planes of symmetry.

Crystallographic Axes.—Three unequal, noninterchangeable, mutually perpendicular axes, usually oriented as shown in Fig. 189.   The longest axis is the c axis, and it is generally the vertical axis.   The longer of the two remaining axes is the *macro* or b axis, and it is placed from left to right.

The shortest a or *brachy* axis points toward the observer.

Classes.

Class 8 $3A_2$ and $3P$ Bipyramidal.   (Holohedral, or normal.) (Figs. 190, 191.)
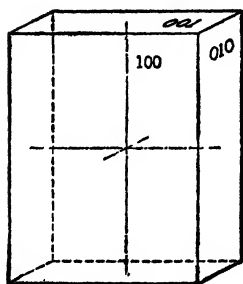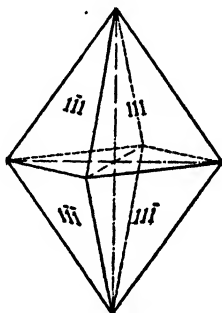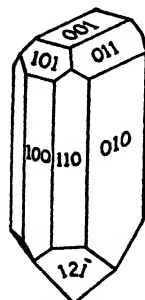
Fig. 190.   Fig. 191.   Fig. 192.   Fig. 193.

Class 7 $1A_2$ and $2P$ Pyramidal.   (Hemimorphic.)   (Figs. 192, 193.)

Class 6 $3A_2$ Bisphenoidal or sphenoidal.

(For Class 7, the vertical c axis is always the axis of twofold symmetry.)

Nomenclature of Faces.—In the orthorhombic system, the existence of three noninterchangeable axes necessitates some means of

distinguishing between various types of pinacoids and domes. The nomenclature employed is as follows:

A *basal pinacoid* cuts the *c* axis.   (001.)

A *macropinacoid* is parallel to the macro and *c* axes.   (100.)

A *brachypinacoid* is parallel to the brachy and *c* axes.   (010.)

A *macrodome* is parallel to the macro-axis.   (101.)

A *brachydome* is parallel to the brachyaxis.   (011.)

Microscopic Views.—No special features exist to distinguish crystals of this system.   Lath-shaped crystals are common. Those interfacial angles which are not right angles are characteristic of the chemical species.   Note that the interfacial angles in zones parallel to an axis of symmetry are unlike unless they are right angles.

149. The Monoclinic System (Clinorhombic, Monosymmetric). *Symmetry.*—Only one axis of twofold symmetry or a plane of symmetry, or both.

Crystallographic Axes.—Three unequal, noninterchangeable axes, one of which is at right angles to the other two, which are oblique.
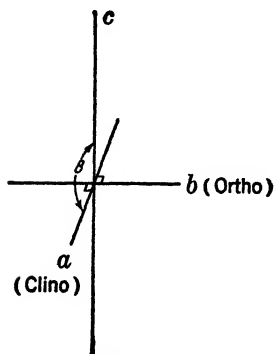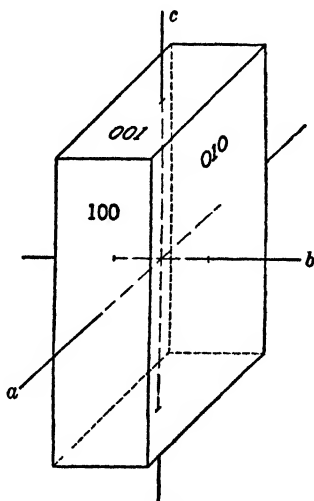
FIG. 194.   FIG. 195.

The axes are oriented as in Fig. 194.   The *b* axis, which is the single axis of symmetry, or *ortho*axis, is always placed from left to right, the *c* axis is vertical, and the inclined *clino*axis *a* dips down toward the observer.

Classes.

Class 5 $1A_2$ normal to P   Prismatic.   (Holohedral, or normal.)   (Figs. 195 and 196, 199.)

Class 4 $1A_2$, no other symmetry   Sphenoidal or hemimorphic.   (Fig. 197.)

Class 3   1P   Domal.   (Domatic or clinohedral.)   (Fig. 198.)

Nomenclature of Faces.—Because of the existence of noninterchangeable axes, it is necessary to distinguish between two
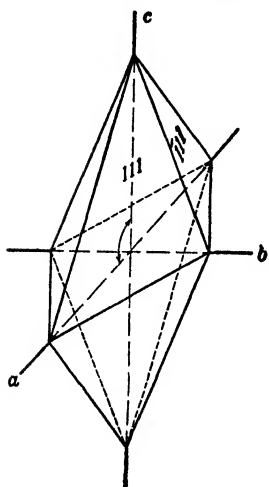
Fig. 196.
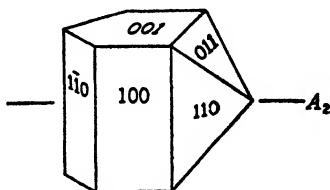
Fig. 197.

forms of pinacoids or domes.   The forms are named according to the following system:

An orthopinacoid is parallel to the ortho and c axes.   (100.)

A clinopinacoid is parallel to the clino and c axes.   (010.)

An orthodome is parallel to the orthoaxis.   (101.)

A clinodome is parallel to the clinoaxis.   (011.)

Fig. 198.

Fig. 199.

Fig. 200.
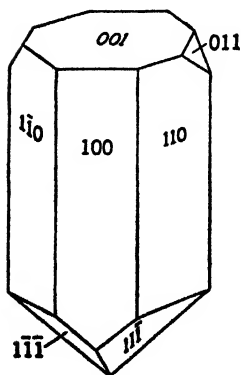
Microscopic Views.—Lath-shaped crystals, parallelograms, and needles are common.   Interfacial angles are characteristic of the species and should always be measured.

150. The Triclinic System (Anorthic, Clinorhomboidal, Asymmetric).

Symmetry.—No symmetry or a center of symmetry

Crystallographic Axes.—Three unequal axes, all oblique.

$$b \wedge c = \alpha, \qquad a \wedge c = \beta, \qquad a \wedge b = \gamma$$

($\wedge$ = "makes an angle with") $\alpha \neq \beta \neq \gamma$. The axes are customarily oriented as in Fig. 200. The longest axis is chosen as
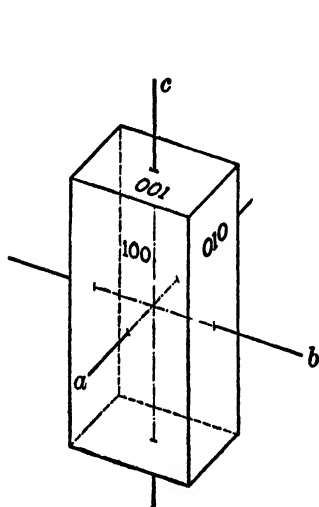
FIG. 201.
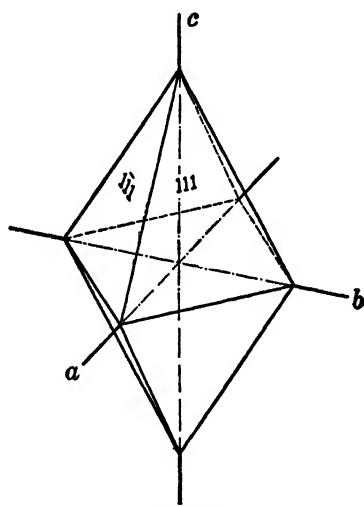
FIG. 202.

the *c* axis and is placed vertical.   The longer of the remaining axes is the *macro*-axis *b* and slopes toward the observer's right. The shortest or *brachy*axis *a* slopes toward the observer's feet.

Classes.

Class 2   Center of symmetry ($1A_2$ (c) and cP)   Pinacoidal or normal.   (Figs. 201 and 202.)

Class 1   No symmetry   Asymmetric.

Nomenclature of Faces.—Same as for orthorhombic system. Note that for crystals belonging to Class 1 a single face constitutes a form.

Microscopic Views.—Characterized by absence of right angles. Rhombs common, also laths and needles. Six- and eight-sided figures occasionally seen; usually irregular.

HABIT

151. The habit of a crystal has already been defined (Sec. 134) as the grouping of possible faces which the crystal "selects"

Platy, lamellar or micaceous

Tabular

Equant

Prismatic or Columnar

Bladed or lath shaped

Acicular or needle-like
(if very thin, the term fibrous is used)
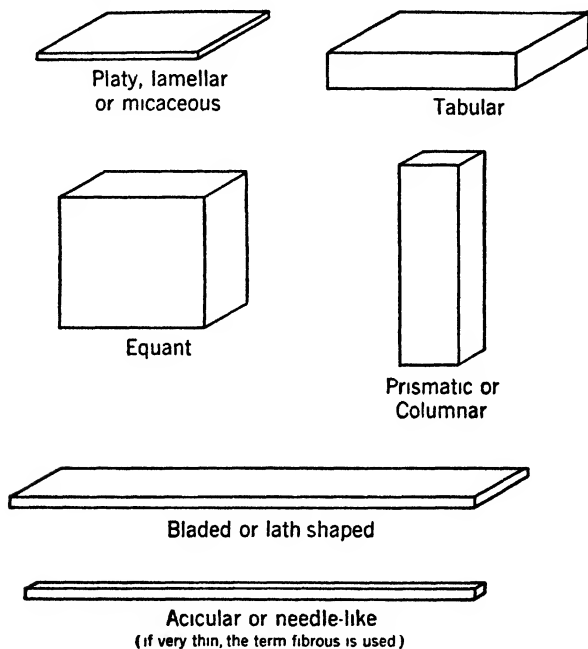
Fig. 203.—Habit.

while growing. The term is somewhat more general in meaning, however, and might well be defined as "data that complement the crystallographic classification." Thus, a crystal may be described as monoclinic and of the prismatic class, with $\beta = 63°$, and yet this gives practically no idea of what the crystal looks like, what faces are prominent, or whether the crystal is flattened or needlelike. The following terms are used to supply such information.

Six typical habits with their common names are shown in Fig. 203. In addition, crystals may form treelike patterns known as dendrites, such aggregates being termed *dendritic* or

arboraceous. If the aggregate is composed of tiny crystals radiating from a center, it is called a *spherulite* or *rosette.* In accounting for these manifold forms, the three controlling factors that determine the habit of a crystal are as follows:

1. Rate of deposition during growth. Rapid deposition on a face encourages formation of a point.

2. Shielding of certain faces. If a face is in contact with the walls of a container, it usually becomes very large.

3. Composition of the mother liquor. For example, addition of urea to sodium chloride solutions causes the salt crystals to change from cubes to octahedra.

152. Other characteristics that should be included in a description of a crystal are the color and the type of cleavage. The latter term is used for the most part for describing large crystals and refers to those directions or planes along which the crystal splits or may be cut most easily. The cleavage plane is always parallel to a plane of the space lattice in which the atoms are densely packed, and hence it is always parallel to an actual or incipient crystal face. The cleavage plane is defined by its Miller indices.

Fig. 204.

A typical description of a crystal might read as follows, and should be accompanied by a sketch (see Fig. 204):

System—Monoclinic $a:b:c = 0.6124:1:2.689$ $\beta = 99°$.

Class—Prismatic.

Color—Colorless.

Habit—Well-formed columnar or tabular crystals, elongated along the c axis, showing clinopinacoid {010}, clinodome {011}, and prism {110}.
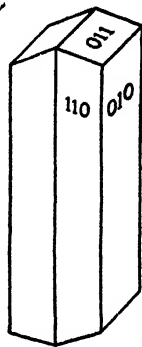
TWIN CRYSTALS

153. Two crystals of the same chemical substance occasionally grow together to form a *twin crystal.* This union of two (or more) crystals may appear as growth of one crystal on some face of the other, in which case the combination is called a *contact twin,* or the two crystals may interpenetrate one another to form *penetration twins.* If the two components of the twin are so related that they may be made to coincide by rotation about an

axis, the pair shows *rotation twinning* about a *twinning axis*. If the components may be brought to coincidence by reflection through a plane, the latter is called a *twinning plane* and the twins are called *reflection twins.* A third type of twinning results from a combination of the preceding two types and is known as
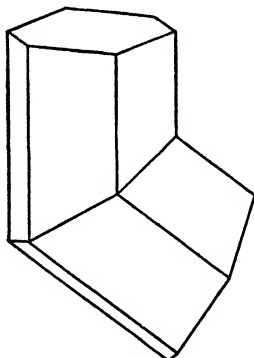
FIG. 205.
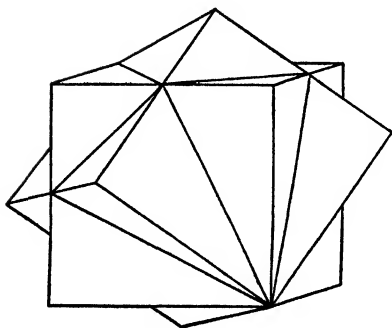
FIG. 206.
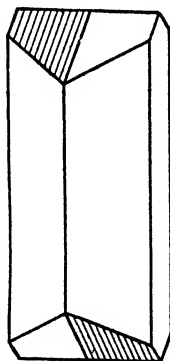
FIG. 207.

inversion twinning or *point twinning.* Several types of twins are shown in Figs. 205 to 207.

EXPERIMENTAL

1. Examine a collection of crystal models, and group them according to their systems. Base your choices on both the determination of partial symmetry and choice of crystallographic axes.

2. Classify the members of the various systems according to whether a given crystal is of the holohedral class or of a lower grade of symmetry.

3. Orient several crystals with respect to the crystallographic coordinate axes; name and give the Miller index of all faces.

4. Examine under the microscope crystals of alum (isometric), nickel sulfate tetrahydrate (tetragonal bipyramid), potassium dihydrogen phosphate (tetragonal prism), strontium chloride (hexagonal), sodium nitrate (rhombohedral), potassium nitrate (orthorhombic), silver nitrate (orthorhombic), sodium sulfate decahydrate (monoclinic), succinic acid (monoclinic), copper sulfate (triclinic).

NOTE: The preparation of microscope slides of crystals may be carried out in several ways, depending upon the particular materials, but the following procedures are of more or less general application:

Place the thoroughly cleaned slide on a warm copper block, add a minute amount of solid, and dissolve the latter in a drop of distilled water. Allow to evaporate until a crust forms at the edges, then stir the crust into the center of the drop until it almost dissolves. Remove subsequent crusts in the same way until the crystals in the center of the drop are sufficiently developed. Remove mother liquor with a sliver of hardened filter paper or a fine glass capillary. Recrystallize if necessary by drawing a tiny drop of water around the edge of the mass and allowing it to evaporate. If masses and aggregates form, too much material was used or else the slide was not sufficiently clean to permit spreading of the drop. Larger crystals may sometimes be obtained by slower evaporation of the drop. This may be accomplished by placing the slide in a small desiccator containing saturated aqueous lead nitrate ($PbNO_3 \cdot 5H_2O$) or sodium carbonate ($Na_2CO_3 \cdot 10H_2O$) which maintain a high humidity.

When using volatile solvents, it is usually necessary to cover the slide with an inverted crystallizing dish to prevent too rapid evaporation. If the drop of solvent shows too great a tendency to spread, the crystallization is best conducted in a microbeaker or small test tube. The fine crystals obtained by relatively rapid cooling or evaporation are centrifuged off or filtered off in a micro buchner funnel. For further information, see Chamot and Mason[5] or Barker,[12] and for methods used in organic chemistry see Morton.[6]

PROBLEMS

1. Describe the following crystals according to the form given in Sec. 152. Data may be obtained from references cited at the end of the chapter. Give a sketch wherever possible.

$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ .... Di-*o*-nitro-di-succinanilide
$K_2Mg(SO_4)_2 \cdot 6H_2O$ .... *o*-Chlorobenzamide
$K_2Cu(SO_4)_2 \cdot 6H_2O$ .... Oxalic acid

2. Taking as a basis the elementary laws of crystallography stated or implied in this chapter, prove that there cannot be an axis of eightfold symmetry.

3. Sketch a crystal having the following description: Orthorhombic, holohedral class, consisting of well-defined columnar crystals showing

principally {001, 010, 110}. Forms {111} and {100} developed to slight extent.

4. Give the Miller indices and names of all the faces belonging to the following forms (holohedral):

(a) Tetragonal {111}.

(b) Orthorhombic {111}{100}{011}.

(c) Monoclinic {101}{110}.

(d) Triclinic {111}{101}.

5. If a completely developed crystal has a mirror image which is not identical with it, to which of the seven systems may it belong?

6. Make a rough sketch of a simple crystal belonging to Class 19 (bipyramidal, trigonal system).

REFERENCES

1. J. W. Evans and G. M. Davies, "Elementary Crystallography," Thomas Murby and Co., London, 1924.

2. N. H. Hartshorne and A. Stuart, "Crystals and the Polarizing Microscope," Edward Arnold & Co., London, 1934.

3. A. Johannsen, "Manual of Petographic Methods," McGraw-Hill Book Company, Inc., New York, 1932.

4. C. S. Hurlbut, Jr., "Dana's Manual of Mineralogy," John Wiley & Sons, Inc., New York, 1941.

5. E. M. Chamot and C. W. Mason, "Handbook of Chemical Microscopy," John Wiley & Sons, Inc., New York, 1938.

6. A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Company, Inc., New York, 1938.

7. E. H. Kraus, W. F. Hunt, and L. S. Ramsdell, "Mineralogy," McGraw-Hill Book Company, Inc., New York, 1936.

8. A. C. Shead, *Ind. Eng. Chem. Anal. Ed.*, **29**, 496 (1937).

9. P. Groth, "Chemische Krystallographie," W. Engelmann, Leipzig, 1919.

10. T. V. Barker, "Systematic Crystallography," Thomas Murby and Co., London, 1930.

11. A. C. Shead et al., *Ind. Eng. Chem. Anal. Ed.*, **9**, 496 (1930); *cf. Chem. Abstracts*, **32**, 2869 (1938); **33**, 88 (1939); **35**, 1287 (1941).

12. T. V. Barker, "The Study of Crystals," Thomas Murby and Co., London, 1930.

13. A. N. Winchell, "Microscopic Characters of Artificial Solid Substances or Artificial Minerals," Part II, John Wiley & Sons, Inc., New York, 1931.

CHAPTER VI

IDENTIFICATION OF CRYSTALS WITH THE POLARIZING MICROSCOPE

154. It is apparent from the preceding chapter that identification of crystalline substances by their outward or geometrical characteristics, such as class, habit, and interfacial angles, is not an altogether easy matter. Also, the relatively large specimens of well-developed crystals necessary for the study are not always obtainable. However, the identification of crystalline materials by means of their optical properties is fairly easy to carry out and requires only a few milligrams of sample, which may even be in the form of a powder (particles > 0.05 mm.).

OPTICAL PROPERTIES OF ISOTROPIC MATERIALS

155. In order to provide a foundation for the discussion that follows, it is necessary to review a few fundamentals and definitions from elementary optics.

1. Light is a form of energy which for the present purpose is considered as transverse waves or vibrations traveling at about 186,000 miles/sec. in a vacuum. The wave length of the vibration determines the color of the light.

2. The velocity of light in a transparent substance is characteristic of the substance and is less than the velocity in a vacuum. Further, the velocity of light in any substance is dependent on the wave length of the light, the velocity of red light being greatest.

3. The refractive index of a substance is the ratio of the velocity of monochromatic light in a vacuum to the velocity in the substance

$$n = \frac{v \text{ (in vacuum)}}{v \text{ (in substance)}}$$

4. Owing to this difference in velocity, a ray of light is bent when it passes obliquely from one medium into a second medium of different refractive index. The fundamental equation

expressing this fact is

$$n = \frac{\sin i}{\sin r}$$

where i is the angle of incidence and r is the angle of refraction, both angles being measured from the normal to the boundary between the two media. It follows from paragraph 2 that the refractive index is a function of the wave length or the color of the light; short waves are bent most, and a substance shows its highest refractive index for violet light, its lowest refractive index for red light.

5. An isotropic substance is a substance that has only one refractive index, *i.e.*, it transmits light with equal velocity in all directions. Isotropic substances include gases, liquids, glasses, and crystals of the isometric system, *e.g.*, NaCl or KI.

156. Measurement of the Refractive Index of Solid Isotropic Substances.—If powdered glass ($n = 1.5$) is suspended in water

$n_1 \neq n_2$ $n_1 = n_2$

FIG. 208.

($n = 1.3$), the outlines of the grains are easily seen because the illuminating light is bent or refracted and scattered as it passes from the water into the glass. If, however, the powdered glass is suspended in a medium that has exactly the same refractive index as the glass, the light will not be bent in passing from one medium to the other, the suspension will be optically homogenous, and the particles will be invisible (see Fig. 208).

The obvious conclusion which may be drawn from this experimental fact is that in order to measure the refractive index of a powdered isotropic substance, it is necessary to suspend the sample in a series of liquid media of known refractive index, until a medium is found in which the particles become invisible. The procedure may be carried out on a series of microscope slides, in the following manner:

Experimental.—The sample is crushed in an agate mortar, or, if friable, upon a microscope slide. A few grains are sprinkled over a small area on a clean slide and are covered with a ⅜- to ½-in. cover glass. A drop of mounting medium, adhering to a

glass rod, is brought in contact with the slide a short distance from the edge of the cover glass so that it flows under the latter by capillary attraction. The immersed grains are then examined under the microscope. The long-focus condenser used should be stopped down and lowered so as to give a narrow, almost parallel pencil of light. Use a yellow filter. Examine powdered glass ($n = 1.515$) in media 1.510, 1.520, 1.515, or sodium chloride ($n = 1.544$) in media 1.540, 1.550, 1.545. Either the 16- or the 4-mm. objective may be used. (Save the slides for the next two experiments.)

157. The Becke Line.—When a crystalline fragment shaped roughly like a convex lens is immersed in a liquid of *lower* refrac-

Fig. 209.

tive index, the fragment tends to converge light, as does a convex glass lens in air. When such a particle is illuminated by a narrow beam of parallel light and observed under the microscope, it appears to be surrounded by a bright fringe, or "halo," known as the Becke line. When the microscope is focused upward by raising the tube, the halo appears to move inward toward what may be called the focal point of the lens particle. If the refractive index of the particle is less than that of the medium, the particle acts as a diverging lens and the Becke line moves outward as the objective is raised. This phenomenon is illustrated in Fig. 209. The Becke line is shown not only by fragments of the type illustrated, but also by crystals with vertical edges, *e.g.*, NaCl (Fig. 210), and by spheroidal droplets such as oil globules or bubbles. The optical theory of the former case has been the subject of some misunderstanding. The correct explanation is given by Saylor.[1] The utility of the Becke line as a guide to the determination of refractive index by the immersion method

is summed up in the following rule: On raising the focus of the microscope, the Becke line moves toward the medium of the higher refractive index.

Experimental.—Reexamine the slides of powdered glass or sodium chloride mentioned above, and observe the movement of the Becke line. The 10× objective and low-power condenser should be used. The condenser is lowered and the iris stopped

Objective lowered   Objective raised
Fig. 210.—Appearance of NaCl ($n = 1.544$) in medium 1.540.

down to give a narrow cone of rays approximately focused on the object. Try the 45× objective also. The habitual use of a yellow filter is recommended. Use of a sodium-vapor lamp gives even better results.

158. The Half-shadow Method.—A similar method of discovering whether the refractive index is higher or lower than that of the surrounding medium is provided by shading half the field

Black   Blue

Brown-
red

$n_{particle} < n_{medium}$ $n_{particle} = n_{medium}$ $n_{particle} > n_{medium}$
Fig. 211.—The half-shadow test.

of view of the microscope and noting which side of the particle is shaded. (Use white light.) If the particle is shaded on the same side as the microscope field, then the particle has the higher index. Conversely, if the shading is on the opposite side, the particle has a lower index than the medium (Fig. 211). The shadow is customarily produced by inserting a card below the substage so that about four-fifths of the objective aperture is darkened. Alternatively, if the microscope is provided with a

sliding analyser or a body-tube slot for a compensator, the analyser or compensator may be pushed halfway in to darken part of the field.   Whatever the means used to shadow the field, it is necessary that the particle be at or above the focal point of the condenser, or the effects will be reversed.[1]   The condenser should be lowered, and a low-power objective should be used. Under ideal conditions, it is possible to measure refractive indices to ±0.0005 by the Becke and half-shadow methods, although in practice the error may be as much as ±0.002.

When the index of the particle is fairly close to that of the medium, the shadings observed in the particle may be colored. The appearance of a light blue border on the "bright" side and a

FIG. 212.—Explanation of the half-shadow test.

pale red or brown border on the shadow side indicates that the refractive index of the particle and the medium are the same for yellow light.   An accuracy of roughly ±0.001 may be achieved by this test under usual conditions, provided that the dispersion of the liquid is not too great.

The theory underlying the appearance of the tints is simple and involves two facts: (1) that the dispersions of liquids is generally greater than that of solids, and (2) that the refractive index of any substance is greater for blue than for red light.   Thus in the preceding case, if the refractive index of the fragment is equal to that of the medium for yellow light, then the medium will have the larger index for blue light and the smaller index for red light. If the particle were illuminated with red light, it would be shaded on the same side as the field, whereas if illuminated with blue

light, it would be shaded on the opposite side.   When illuminated with white light, which is composed of all colors, the fragment will appear bluish at one edge and red at the other.   Since the phenomenon depends on the relative dispersive powers of the fragment and the immersion medium, it is not always observable.

The observation that the Becke line disappears as the substage diaphragm is opened was put to good use by Viola,[8] who worked out the relation

$$n_1 = kD^2 - n_2$$

where n, and n_2 are the indices of particle and medium (or vice versa), D is the diameter of the diaphragm opening (in millimeters), which will just cause the Becke line to disappear, and k is an experimentally determined constant for the microscope.

Fig. 213.—Simple schlieren cell.

Experimental.—Examine powdered glass in prepared mixtures of neutral oil and α-bromonaphthalene: $n = 1.510, n = 1.515$, and $n = 1.520$.   Note the half-shadow tints and the relative positions.   Try the Becke test also.

159. Determination of the Refractive Index of Liquids.—It might be noted here that the preceding tests apply to liquids in capillary tubes as well as to solid fragments.

The so-called schlieren test[2,3,4] depends on the same principle as the half-shadow method and is carried out as follows:

A specially prepared flat-walled cell is used, which may be constructed from ordinary microscope slides and Lucite (Fig. 213).   The microscope is placed in a horizontal position and adjusted for oblique illumination as above.   The cell, containing a liquid of known refractive index, is fastened to the stage, and a tiny capillary pipette, containing the liquid of unknown index, is introduced into the cell so that its tip is below the surface of the medium.   As the unknown liquid slowly flows into the medium, a striation or schlieren current forms.   This is observed through the microscope, and the shading is noted as for the half-shadow test on solids.   A microscope equipped with special half-shadow diaphragms is used for more precise determinations

(see Saylor[1]). By this means, the refractive index of exceedingly minute samples may be determined to approximately ± 0.0005. The method is also applicable to density determinations, since the schlieren current will move either up or down, depending on whether the added liquid is lighter or heavier than the medium of known density.

Emich[2] cites the utility of the method for determining the concentration of a solution by observing a series of schlieren in prepared solutions of known concentration. It may also be used for determining the purity of a liquid, either by comparison with a known sample or with a distillate of the suspected liquid, conveniently obtained by microdistillation in an Emich tube.[2]

160. The Double-variation Method.—This method of determining the index of refraction is exactly the same in principle as the simple Becke method, but it gives additional information and is capable of greater accuracy. The distinguishing feature lies in the use of comparatively few immersion media, whose refractive indices are varied by changing the temperature and the wave length of the monochromatic illumination used (see tables in Winchell[6]).

In practice, a special hollow slide is employed, whose temperature is maintained at any desired level by a stream of warm water, which is also conducted through the hollow prism casing of an Abbe refractometer (Sec. 201). The source of illumination for both microscope and refractometer is a monochromator of high intensity. The fragment of unknown material is placed on the slide and mounted in some liquid of nearly the same refractive index. A drop of the same liquid is placed in the refractometer. While maintaining a given temperature, the wave length is adjusted until the Becke line of the particle disappears, when the index of the mounting liquid is read from the refractometer.

Several such match points are determined at various wave lengths by changing the temperature, so that the dispersion curve of the particle may be plotted (n vs. λ) (see Fig. 214). The index of refraction n_D for the sodium line (5,893 A) may be read from this curve and also the dispersion $n_F - n_C$ or $n_{Tl} - n_{Li}$ where F and C refer to the blue and red lines of the hydrogen spectrum (4,861 A, 6,563 A) and Tl and Li refer to the thallium and lithium lines (5,351 A, 6,708 A). It is assumed that the index

of the solid does not change appreciably with temperature. The dispersion, incidentally, is a characteristic constant which is of diagnostic value.

Owing to the expense of the necessary equipment, the refined method described above is not likely to become popular as such. It is possible, however, to economize, with some sacrifice of accuracy, by dispensing with both monochromator and refractometer. The monochromatic light may be supplied by a mercury arc or incandescent lamp used with suitable filters, and according to Emmons,[5,6] the n vs. T and n vs. λ curves for the

FIG. 214.—Typical data from the double-variation method. The curve $ABCD$ shows the relation of the refractive index n of a particle to the wave length λ. From this curve the refractive index at the standard wave length 589 $m\mu$ may be obtained, as well as the standard dispersion $n_{487} - n_{656}$.

various media used may be plotted once and for all when the liquids are made up. These media are for the most part pure liquids whose properties do not vary over long periods of time.

161. Experimental.—Referring to the table of refractive indices at the end of the chapter identify an isotropic crystal by the following procedure:

Crush the material, and place a few milligrams in a small, approximately 100-mesh sieve. (The small sieves used to filter tap water serve very well.) Tap the sieve so that a half dozen grains fall in a small area on a microscope slide. Place a ½-in. cover glass over the particles, introduce a drop of immersion medium, and examine under the microscope. Note the relief or distinctness of the particles. If they stand out clearly, appear dark, opaque, or rough, their index is probably considerably

different from that of the medium.   Using the Becke test as a
guide, make up another slide in a different medium.   Repeat
the process until the Becke and half-shadow tests show that the
indices are within 0.005.   By taking the next higher or lower
medium, it is possible to estimate the index to about 0.002.   In
precise work, it is advisable to check the index of the final medium
with a refractometer.   After some experience, it should not be
necessary to make more than three or four trial slides.

162. Immersion Media.—The series of liquids used for deter-
mining the refractive index of particles by the simple immersion
method has been the subject of considerable research, since the
accuracy of a determination depends largely on the medium used.
The properties of an ideal series are discussed by Buerger.[7]

In the following paragraphs, some of the usual mixtures are
described.   For a more comprehensive summary, see Johannsen[8]
and Chamot and Mason,[9] who list media up to $n = 2.70$.

TABLE 14 —MIXTURES USED AS IMMERSION MEDIA

Range	Components	Reference
1 355–1 460	Petroleum distillates	2, 7
1 411–1.466	Government oil and *n*-decane	6
1 429–1.456	Petroleum distillates	3
1 384–1 498	Ethyl propionate and mesitylene	4
1.423–1.658	Heptylic acid and α-bromonaphthalene	4
1 493–1.658	*n*-Butylphthalate and α-bromonaphthalene	4
1.460–1.632	Kerosene and α-chloronaphthalene*	7
1 633–1.658	α-Chloronaphthalene and α-bromonaphthalene	
1.633–1.739	α-Chloronaphthalene and methylene iodide	6
1 739–1.780	Methylene iodide and sulfur	6
1 780–1.800	Above plus tetraiodoethylene	
1 800–1 843	Above plus phenyldiiodoarsine	5
1.780–1 960	Methylene iodide, sulfur, and sulfides	9

* Commercial Halowax is suitable.

The media listed in Table 14 are designed primarily for use in
determinations of inorganic materials and may be unsuitable for
determining the refractive index of organic compounds which are
soluble in many of the liquids.   Several series of aqueous mixtures
have been devised for the latter purpose, as well as mixtures of
oils having low solvent power.

Glycerol may be advantageously substituted for water in the
last three mixtures in Table 15, since it reduces the volatility.

This advantage is offset by its hygroscopic property, which, however, is serious only in humid atmospheres.

In making up any one of the sets of media given in Table 14 and Table 15, it is advisable to use 15-ml. brown-glass bottles with ground-in droppers and ground-glass caps. Some mark should be made on the label to indicate the components of the mixture. The bottles are conveniently kept in a wooden block drilled with holes of suitable size, and the set should be kept in a lighttight box or drawer.

TABLE 15.—AQUEOUS IMMERSION MEDIA

Range	Components	Reference
1 335–1.400	Water, glycol, glycerol	12
–1.610	Water, glycerol, zinc iodide	
–1.700	Water, cadmium borotungstate	8
–1.720	Water, potassium mercuric iodide	8
–1.793	Water, barium mercuric iodide	8

The lower nonaqueous media are prepared by fractionally distilling petroleum ether, through a packed column, and blending adjacent fractions to the desired index. These media are very volatile, but their index does not change on evaporation. For liquids above $n = 1.430$, the simpler procedure of Bosazza[10] is recommended. Kerosene (flash point = 300°F.), which is free from objectionable odor, is distilled in a tall-necked distilling flask, and the desired fractions are collected.

So-called "government oil" is a petroleum fraction that is quite pure and nonvolatile. It is blended with α-chloronaphthalene (trade name Halowax) according to the mixing curve given by Kaiser and Parrish.[11] These authors also give mixing curves for α-chloronaphthalene and methylene iodide and for methylene iodide and sulfur.

The equation $n(V_1 + V_2) = n_1 V_1 + n_2 V_2$ serves as a rough guide to the preparation of binary mixtures of index n, from volumes V_1 and V_2 of the end members whose indices are n_1 and n_2, respectively. The indices are read from an Abbe or other refractometer and should be within ± 0.0005 of the index recorded on the bottle. For methods of measuring high refractive indices, see Chap. VII.

TABLE 16.—REFRACTIVE INDEX MEDIA*

	N_D 20°C.
Methyl alcohol	1.3288
Water	1.3330
Acetone	1.3592
Ethyl acetate	1.3727
n-Hexane	1.3755
n-Heptane	1.3872
n-Butyl alcohol	1.3991
n-Butyl chloride	1.4022
1, 4-Dioxane	1.4223
Methyl cyclohexane	1.4235
Ethylene glycol	1.4318
Ethyl citrate	1.4434
Ethylene chloride	1.4453
Trimethylene chloride	1.4476
Cyclohexanone	1.4507
Cyclohexanol	1.4678
Diethanolamine	1.4782
Triethanolamine	1.4853
p-Cymene	1.4908
s-Tetrachloroethane	1.4943
Toluene	1.4957
Benzene	1.5017
Ethyl iodide	1.5138
Anisole	1.5178
Trimethylene bromide	1.5238
Chlorobenzene	1.5250
Methyl iodide	1.5310
Ethylene bromide	1.5383
o-Nitrotoluene	1.5466
Nitrobenzene	1.5526
Tri-o-cresyl phosphate	1.5582
Bromobenzene	1.5602
o-Toluidine	1.5725
Aniline	1.5864
Bromoform	1.5973
o-Iodotoluene	1.6095
Quinaldine	1.6120
Iodobenzene	1.6205
Quinoline	1.6272
s-Tetrabromoethane	1.6378
α-Bromonaphthalene	1.6585
Methylene iodide	1.74

* Sold in 25-ml. bottles by the Eastman Kodak Company (indices as given).

ANISOTROPIC CRYSTALS

163. The foregoing discussion has been confined to isotropic substances which transmit light with equal facility in any direction. The great majority of crystalline materials, however, are anisotropic, or nonisotropic, and transmit a ray of light with varying velocity according to the direction of the ray in the crystal. Since the refractive index depends on the velocity of

Fig. 215a.—Unpolarized
light.

Fig. 215b.—Polarized
light.

light in the substance, it follows that the refractive index of an anisotropic crystal depends on the orientation of the crystal. Crystals may be classified according to the number of distinguishable and characteristic refractive indices that they exhibit.

TABLE 17.—OPTICAL CLASSIFICATION OF CRYSTALS

Isotropic	Anisotropic	
	Uniaxial	Biaxial
One refractive index n	Two refractive indices ω and ϵ	Three refractive indices α, β, and γ
Isometric crystals, liquids, and glasses.	Tetragonal, hexagonal, and r h o m b o h e d r a l crystals	Orthorhombic, monoclinic, and triclinic crystals

164. Polarization of Light by Anisotropic Crystals.—Before undertaking the study of anisotropic crystals, it is necessary to review the concept of polarization of light. An especially clear and simple discussion of polarized light is given by Robertson.[18] For the present purpose, it is sufficient to describe light as a wave motion whose waves or vibrations are normal to the direction of propagation and which are in a family of planes including the

direction of propagation.   A hypothetical view of a ray of light traveling perpendicular to the plane of the paper is shown in Fig. 215a.

C axis —— Uniaxial crystal

FIG 216.

Plane polarized light is light whose vibrations have all been brought into one plane, as shown diagrammatically in Fig. 215b.

Plane polarized light may be produced in several ways:

1. By partial reflection, as from a sheet of glass or polished desk top, also by reflection (scattering) from colloidal particles.

2. By means of the Nicol prism and related devices.

3. By means of pleochroic anisotropic crystals, *e.g.*, tourmaline and iodo-quinine sulfate. (*Polaroid* consists of tiny, needle-like crystals of the latter substance mounted in a plastic base which is then stretched or otherwise processed so that the crystals are lined up with their long directions substantially parallel.)

C axis

FIG. 217.

When unpolarized light enters a uniaxial crystal, *e.g.*, calcite ($CaCO_3$, rhombohedral), the various layers of ions in the crystal lattice somehow *resolve* the heterogenous light vibrations into two mutually perpendicular planes.   Note that the process is one of resolution and that no rays are filtered out.   Figures 216 and 217 show how one of the random light vibrations AA' is resolved on entry into a crystal into its components OO' and EE'.

The resolution takes place at the moment of entry into the crystal, and the net effect is the production of two polarized rays, vibrating in mutually perpendicular planes. These two rays then proceed through the crystal with unequal velocities, and hence the crystal exhibits two refractive indices, a low refractive index for the faster ray, a high refractive index for the slower ray. One of these rays vibrates in a plane which includes the direction of propagation of the ray and the c axis of the crystal, and since this ray exhibits anomalous behavior, it is known as the *extraor-*

Fig. 218.

Fig. 219.—The Nicol prism.

dinary ray. The other, the *ordinary* ray obeys the usual laws of refraction and vibrates in a plane including the direction of propagation and perpendicular to the plane of the c axis.

Since the refractive index of the crystal is less for one ray than for the other, the two rays will proceed along different directions in the crystal after refraction at an inclined surface. This is illustrated in Fig. 218, which shows the passage of the two polarized rays through a rhombohedron of calcite.

165. The Nicol Prism.—In order to obtain a ray of pure polarized light, it is necessary to get rid of one of the two rays indicated in Fig. 218. This separation of a single ray is accomplished in the Nicol prism (Fig. 219) by total reflection of the

ordinary ray from a film of Canada balsam.   The Nicol prism is constructed from a natural crystal of calcite by grinding the original rhomb faces to an acute angle of 68°.   The rhomb is then cut in two, and the halves are cemented together again with Canada balsam.   Balsam is chosen because its refractive index (1.54) is intermediate between the refractive index for the extraordinary ray (1.486) and the ordinary ray (1.658).   Light enters the crystal as shown, and is resolved at once into the extraordinary ray (the fast ray in the case of calcite) and the slow, ordinary ray.   These rays pursue different courses through the crystal and impinge on the Canada balsam layer. Here, the extraordinary ray goes from a medium of low refractive index into a medium of higher refractive index and is therefore refracted slightly toward the left (Fig. 219), whereas the ordinary ray passes from a medium of high refractive index into a medium of lower refractive index.   The angles of the prism have been adjusted so that the ordinary ray strikes the balsam interface at an angle slightly greater than the critical angle and is therefore totally reflected out to the side.   The extraordinary ray, however, traverses the balsam layer and the second portion of the prism, from which it emerges as plane polarized light vibrating in a plane that is parallel to the optic plane of the calcite.   This plane includes the *c* axis of the crystal and the short diagonals of the end faces, as shown in Fig. 218.

FIG. 220.

If, now, this polarized light enters a second Nicol prism, (Fig. 220) several things can happen, depending on the relative orientation of the optic planes of the two prisms.   If these optic planes are parallel, then the polarized light from the first prism, or polarizer, passes through the second prism, or analyzer, unchanged.   If, however, the optic planes of the polarizer and the analyzer make an angle θ with one another, the original polarized ray will be resolved when it enters the second prism as shown diagrammatically in Fig. 221.   The two resultants FF' and SS' in the analyzer A are the fast and slow rays discussed in the preceding paragraph.   The slow, ordinary ray SS' is rejected at the balsam interface, whereas the fast, extraordinary ray FF' con-

tinues on through the prism.   The amplitude of the ray leaving the analyzer is given by the equation

$$\frac{A}{A_o} = \frac{FF'}{PP'} = PP' \cos \theta$$

where A and A_o represent the transmitted and original amplitudes (FF' and PP', Fig. 221).   Since intensity is proportional to the square of the amplitude, the equation may also be written as $I/I_o = \cos^2 \theta$ where I and I_o are the transmitted and original intensities.   Note that the polarizer P alone transmits just one-half of the entering light and that if $\theta = 90°$ the analyzer will reject all the light from the polarizer, when the two Nicols are said to be "crossed."

Fig. 221.—PP' = vibration plane of light from the polarizer; AA' = optic plane (vibration plane) of analyzer; FF' and SS' = resultants formed in analyzer, of which only FF' is transmitted.

166. The polarizing microscope (Fig. 222) is a microscope equipped with a Nicol prism or Ahrens polarizer (Fig. 223), located below the condenser, and an analyzer that may be mounted in the body tube ("sliding analyzer") or placed on top of the eyepiece ("cap analyzer").   The sliding analyzer is usually of the Ahrens type and is fitted with compensating lenses.   Polaroid disks may be used instead of more expensive prisms, but their faint brownish color is objectionable for many purposes.   Whatever means of polarization is employed, the polarizer should be set in a graduated mounting which allows rotation.   In this text, it will be assumed that the optic plane or vibration plane of the polarizer is normally north-south and that the analyzer is crossed, *i.e.*, its vibration plane is east-west.

In addition to the polarizing apparatus, the polarizing microscope is usually fitted with a rotating graduated circular stage, a special Bertrand lens in the body tube, and an eyepiece that has accurately oriented north-south and east-west cross hairs in the focal plane of the eye lens.

The function of the Bertrand lens will be discussed in Sec. 173, but for the present purpose it may be considered as a means of focusing the ocular on the rear lens of the objective where interference figures (Sec. 173) are located.   It is a convenience rather

EYEPIECE

SPIRAL FOCUSING RING
FOR AMICI-BERTRAND LENS

COARSE FOCUSING ADJUSTMENT

BODY TUBE

MICROMETER-TYPE
FINE ADJUSTMENT

BODY TUBE RACK

QUICK CHANGE
NOSEPIECE

OBJECTIVE
CENTERING
RING

ARM

BALL
BEARING
REVOLV-
ING
STAGE

INCLINATION
JOINT

FORK-TYPE SUBSTAGE
MOUNTING

BASE

STAGE CLIP

FOCUSING EYE LENS

ENGRAVED
CROSS HAIR DISC

EYEPIECE FIELD LENS

AMICI-BERTRAND LENS

COMPENSATING LENS

PROTECTING PLATE

AHRENS
ANALYZING PRISM

PROTECTING PLATE

COMPENSATING LENS

OBJECTIVE LENSES

SWING OUT UPPER
LENSES OF CONDENSER

LOWER FIXED LENSES
OF CONDENSER

UPPER IRIS
DIAPHRAGM

PROTECTING PLATES

AHRENS POLARIZER

MIRROR

LOWER IRIS DIAPHRAGM

Fig. 222.—The polarizing microscope.   (*Courtesy of Spencer Lens Company.*)

than a necessity. Both the Bertrand lens and the sliding analyzer may be swung out of the body tube when they are not in use. Chamot and Mason[9] describe several standard polarizing microscopes in detail and give particulars as to their care and handling. West[20] gives several methods of converting an ordinary microscope to a polarizing microscope through use of Polaroid. All the information on microscopes given in Chap. IV applies to polarizing microscopes as well and should be reviewed at this point. It is especially important that the iris diaphragms, the condenser, the objective, and the ocular be perfectly aligned with the center of rotation of the stage.

167. Use of the Polarizing Microscope—Character of Extinction.—If an isometric crystal, say sodium chloride, is placed on the stage of a polarizing microscope and is examined between crossed Nicols, it is found that both the field of view and the crystal are completely dark. This is so because the internally symmetrical atomic lattice of an isotropic crystal has no effect on the polarized light from the polarizer no matter how the crystal is oriented. Isometric crystals are isotropic and show complete, or *isotropic extinction.*

Fig. 223.—The Ahrens prism.

If, however, a uniaxial crystal such as a pinacoidal, tetragonal, or hexagonal crystal is placed with the *c* axis horizontal on the stage of the polarizing microscope, it will be alternately dark and light, or colored, as the stage is rotated. Further, the crystal will be dark or at extinction when a prominent face or edge is parallel to the north-south or east-west cross hair of the ocular, *i.e.*, when the *c* axis is parallel to the vibration plane of the polarizer or analyzer. At oblique positions, the crystal will be light and usually colored.

The explanation of this phenomenon is easily understood if the behavior of the light in the crystal is considered, as discussed above in the case of calcite. In Fig. 224, a crystal is shown as it appears in the field of view of the microscope. The various

planes of polarization are indicated as vectors. *P* represents the
vibration plane* of the polarized light from the polarizer, whereas
E and *O* represent the vibration planes of the two component rays
formed in the crystal whose *c* axis is so denoted. These two
rays then proceed up through the objective to the analyzer,
which resolves both rays into a resultant vibrating in the plane
A of the optic axis of the analyzer. This resultant passes through
the analyzer to the eye, and the crystal therefore appears light
against a black background.

If the crystal is rotated so that its *c* axis is parallel to the vibra-
tion plane of the polarizer, as in Fig. 225, then no component ray
O can be formed in the crystal, as is obvious from the vectorial

FIG. 224.   FIG. 225.   FIG. 226.

considerations involved. The *E* ray, however, is formed and
continues on up to the analyzer, which rejects it since it has no
component in the east-west vibration plane of the analyzer.
Thus the crystal appears dark against a dark background. The
crystal is likewise "extinguished" when only the *O* ray comes
through, as in Fig. 226. In short, the crystal is at extinction
when the *c* axis is north-south or east-west, whether the axis is
horizontal on the stage or inclined thereto. If the crystal has
edges or faces parallel to the *c* axis, then it will be extinguished
when such an edge or face is parallel to one of the cross hairs.
This is referred to as *parallel extinction*. A rhombohedral,
pyramidal, or domal crystal, on the other hand, will be extin-
guished when the bisector of a silhouette angle is parallel to a
cross hair as shown in Fig. 227. Such extinction is called

* The term *vibration plane* indicates a plane including the direction of
propagation of the ray and the *vibration direction* of the ray in the crystal.
The vibration direction is normal to the direction of propagation and in the
plane of an optic direction, which may be either the optic axis or a normal
thereto.

symmetrical extinction. Note that the bisector of the silhouette angle is in the plane of the c axis irrespective of any distortion of the ideal form of the crystal such as growth parallel to a face, as indicated by the dotted lines in Fig. 227.

Consider now a uniaxial crystal resting on the stage with the c axis vertical. Since the c axis of a uniaxial crystal is the axis of maximum symmetry, the atomic lattice of the crystal as viewed along the c direction shows symmetry comparable to that of the atomic lattice of a cubic crystal. On this basis, it is not surprising to find that a uni-axial crystal affects light traveling in the c direction much as does an isotropic crystal, *i.e.*, the light from the polarizer passes through the crystal effectively unchanged. Since the transmitted ray is "crossed" with respect to the analyzer, the crystal shows complete or *isotropic extinction.* The crystal is dark no matter how the stage is turned. The direction of the c axis of a uni-axial crystal is called the *optic axis* and may be defined for the present purpose as that direction along which a ray of light may travel without the formation of an extraordinary ray. Note that the optic axis is a direction or family of parallel lines, and not a single line. Since no extraordinary ray is formed, a crystal oriented with its optic axis vertical on the stage shows only the refractive index ω characteristic of the ordinary ray.

Symmetrical Extinction
Fig. 227.

Table 18 which lists extinction characters includes biaxial crystals as well as uniaxials, thereby anticipating any theoretical discussion of biaxials. It will be sufficient for present purposes to regard biaxial crystals as similar to uniaxial crystals, with the exception that in the monoclinic and triclinic systems the vibration planes may be inclined to the crystallographic axes, *i.e.*, the optic directions need not be parallel to faces or to the bisectors of face angles. Since a crystal is extinguished when the vibration direction is north-south or east-west, the faces or edges of the

extinguished monoclinic or triclinic crystal need not be parallel to the cross hairs. If the prominent faces or edges of an extinguished crystal make an angle with the cross hairs, the extinction is said to be oblique (Fig. 228). (Compare with symmetrical extinction; avoid confusing the two.)

FIG. 228.—Types of extinction.

In the monoclinic system, there is some correspondence between vibration directions and crystallographic axes in that the b (ortho) axis, which is the single axis of symmetry, is always a vibration direction. For this reason, the monoclinic crystal shows parallel extinction when the b axis is horizontal and oblique extinction when the b axis is not horizontal. In the triclinic system, there is no necessary correspondence between vibration directions and crystallographic axes.

The angle between a prominent face of an extinguished crystal and the nearest cross hair is called the extinction angle (see Fig. 229). Note that this is always less than 45°. It is advisable to measure extinction angles to several faces, and, further, to check the possibility of symmetrical extinction, it is best to measure the profile angles also. Then if the extinction angle is found to be half the profile angle, the extinction must be symmetrical. Conventionally, the maximum extinction angle is the one recorded for purposes of identification or reference.

Extinction angle
FIG. 229.

Two devices are commonly used for exact measurement of extinction angles: the selenite compensator and the Bravais

TABLE 18.—DIFFERENTIATION OF CRYSTAL SYSTEMS BY CHARACTER OF
EXTINCTION

System	Extinction
Isometric	Isotropic or complete
Tetragonal	Parallel or symmetrical. Some isotropic. Latter usually have four-sided silhouette
Hexagonal	Parallel or symmetrical. Some isotropic. Latter usually have three- or six-sided silhouette
Rhombohedral	Symmetrical. Few isotropic. Latter usually are three-sided
Orthorhombic	All show parallel or symmetrical extinction
Monoclinic	Some parallel or symmetrical, some oblique
Triclinic	All oblique

twinned mica plate (Fig. 230). The former, described in Sec. 171, is inserted in a slot above the objective. The crystal is viewed

FIG. 230.—The Bravais plate. (Direction of lines indicates vibration planes.)

through this plate, and when at extinction, the color of the crystal exactly matches that of the plate. The Bravais plate and similar devices are described by Johannsen.[8] These plates are composed of two or more crystal sections mounted in a frame that fits the compensator slot or a slot in the ocular. A crystal at extinction appears the same color in each part of the field, and rotation of as little as 0.3° causes a perceptible change in the color of the two halves.

The determination of system by extinction depends on two assumptions: (1) that many well-formed crystals are involved, and (2) that the crystals are oriented at random, *i.e.*, not all lying on one face.

Experimental.—Examine prepared slides of acenaphthene (orthorhombic), nitroguanidine (tetragonal), copper sulfate pentahydrate (triclinic), potassium chlorate (monoclinic) (note possibility of confusing oblique and symmetrical extinction), lead iodide (hexagonal), sodium nitrate (rhombohedral), ammonium or potassium dihydrogen phosphate (tetragonal), potassium persulfate (triclinic), silver nitrate (orthorhombic), sodium

nitrate (rhombohedral), sodium chlorate (isometric) potassium alum (isometric), and oxalic acid dihydrate (monoclinic).

Determine the character of extinction of an unknown crystal. Sprinkle crystals onto a thin film of tacky Canada balsam or glycerin jelly to ensure random orientation. Examine only the more perfect specimens. If the extinction is oblique, measure the extinction angle for at least a dozen crystals, using the vernier of the rotating stage.

168. The Measurement of Refractive Indices of Uniaxial Crystals.—By referring back to Figs. 225 and 226, it is seen that when a crystal is at extinction only one polarized ray emerges from the crystal and proceeds up to the analyzer, which rejects it. If the analyzer were removed, however, this single ray would continue up to the eye and a light image of the crystal would be seen against a light background. Because of the fact that only one ray emerges from the crystal, however, the crystal will show only one refractive index. If the optic axis of the crystal is horizontal and north-south, then the E vibration or extraordinary ray (Fig. 225) comes through the crystal which therefore shows the refractive index ϵ characteristic of the extraordinary ray. This refractive index can be measured by the immersion methods.

Conversely, if the crystal is oriented with the c axis east-west, as in Fig. 226, then only the ordinary ray comes through the crystal, which then exhibits the refractive index ω characteristic of the ordinary ray. Thus, the method of determining the two refractive indices of a uniaxial crystal is just the same as for isotropic crystals, with the sole difference that in the case of the uniaxial crystal it is first necessary to align the crystal in the proper position.

Experimental.—Nitroguanidine is uniaxial and is elongated along the c axis. Using a slide of nitroguanidine crystals mounted in Canada balsam, place a needle north-south at extinction, *i.e.*, parallel to the vibration plane of the polarizer. Remove the analyzer, and note the movement of the Becke line. Rotate to the east-west position, and again note the movement of the Becke line. Which is larger, ϵ or ω? Does the slow ray vibrate lengthwise or crosswise of the crystal?

Determine the two refractive indices of nitroguanidine or some other acicular uniaxial crystal, such as urea, by the foregoing procedure through the use of suitable immersion media.

169. Note that ϵ (extraordinary ray) may be measured only on crystals whose optic axes are horizontal on the slide and oriented parallel to the north-south vibration plane of the polarizer.   If the optic axis is not horizontal, then ϵ cannot be measured.   The refractive index obtained if the optic axis were tilted in the *north-south plane* would be intermediate between ϵ and ω, and its magnitude would be a function of the degree of inclination of the optic axis.   As the optic axis becomes more nearly horizontal, the observed refractive index approaches ϵ as a limit, and as the

Fig. 231.—Uniaxial index ellipsoid (+).

optic axis becomes nearly vertical, the observed index approaches ω.   Similarly, ω is observable only when the optic normal is horizontal.

The relation between the orientation of a crystal and the observable refractive index is conveniently summarized in the so-called *index ellipsoid* shown in Figs. 231 and 232.   This is an ellipsoid of revolution about axis AC, which is the vibration direction of the extraordinary ray.   The magnitude of the refractive index ϵ for the extraordinary ray is represented by the semi-axis AB.   The length of the semi-axis BG corresponds to the magnitude of the refractive index ω.   Note that BG is a radius of the circular section.

In order to find the relation between the orientation of a crystal and its observable refractive indices, it is customary to visualize such an ellipsoid within a crystal whose c axis corresponds to AC. If the light from the polarizer enters the crystal along the FD

axis of the ellipsoid, it is broken up as we have seen into an extraordinary ray, vibrating in the direction AC, and an ordinary ray, vibrating in the direction GH. The length AB gives the magnitude of the extraordinary ray index ϵ, whereas the index ω, for the ordinary ray, corresponds to the length of the other semi-axis $BG = BD = BH = BF$. Thus, if light travels normal to

FIG. 232.—Uniaxial index ellipsoid ($-$).

the optic axis, both ϵ and ω may be determined. If the optic axis is tilted so that the entering light travels along some direction such as JB, it is resolved, as before, into two rays. The vibration directions of these rays are not the same as before, however, because of the altered orientation of the crystal and because vibration directions must be normal to the direction of propaga-

tion (JB). The extraordinary ray must, by definition, vibrate in a plane including the direction of propagation and the optic axis AC. Thus, the vibration direction of the extraordinary ray will be BK. But the magnitude of the refractive index of the extraordinary ray is given by the magnitude of the vector BK, and, as is obvious, the observed index will be less than ϵ. The ordinary ray, on the other hand, will vibrate in a plane perpendicular to that of the extraordinary ray. Its vibration direction and magnitude are represented by BL. However, since the vibration directions of the ordinary ray are all radii of the circular section, $BL = BG$ and the observed refractive index for the ordinary ray remains unchanged, *i.e.*, the crystal will show the index ω. Similar constructions may be made for any orientation of the crystal, or its "hypothetical inner ellipsoid," that show the magnitude of the observable refractive indices. For the measurement of these indices, of course, the stage must be turned so that the vibration plane of the desired ray is north-south.

At this point, the explanation of the definition of the optic axis becomes apparent if a ray traveling along AC is considered. Such a ray would be resolved into components BF and BG, which are both equivalent to ω. Thus the crystal will exhibit only the index ω regardless of rotation about AC.

Note that the ellipsoid is prolate if $\epsilon > \omega$ and oblate if $\omega > \epsilon$ (see Fig. 232).

170. The Concept of Birefringence and Sign.—The birefringence of a uniaxial crystal is simply the numerical difference $\epsilon - \omega$. This difference is positive if ϵ is larger than ω, and negative if ω is the larger. The sign of the birefringence is called the optic sign or "sign of the crystal." It is an easily measured characteristic which is of diagnostic value.

In Sec. 164, the concept of fast and slow rays was mentioned briefly, and, in repetition, it may be said that the fast ray actually travels faster through the crystal, which then has the lower refractive index for the fast ray. Therefore, if the extraordinary ray of a crystal is the fast ray, then ϵ will be smaller than ω and the sign of the difference $\epsilon - \omega$ will be negative. Conversely, if the extraordinary ray is the slow ray, the sign is positive. To determine the optic sign, it is necessary to find out whether the ordinary or the extraordinary ray is the slow ray.

When light from the polarizer enters a uniaxial crystal that is not at extinction, it is resolved into an ordinary and an extraordinary ray, one of which will be the slow ray. As these two rays go through the crystal, the slow ray lags behind the fast ray, *i.e.*, it is retarded. At the point of emergence from the crystal, the slow ray may lag one wave length of, say, red light behind the fast ray (see Fig. 233). The two rays, shown vectorially in Fig. 234 as *OF* and *OS*, vibrating in mutually perpendicular planes, proceed, in phase, up to the analyzer, which resolves them into rays *OF'* and *OS'*, which are equal and opposite vibrations and which cancel each other. Therefore, the vibrations of red light are eliminated from the white light passing through the

FIG. 233.—Section of a crystal (side view).

system, with the result that the crystal appears bluish green. If the phase difference due to retardation were one wave length of *blue* light instead of red, then blue would be eliminated and the crystal would appear orange. A retardation or phase difference of 2, 3, 4, · · · *n* wave lengths will, of course, produce a similar

FIG. 234.—Schematic view along axis of microscope.

interference when *n* is a whole number. If the wave length of blue light is taken as 450 mμ, then blue light will be removed by interference when the retardation is 450, 900, 1,350, · · · $n(450)$ mμ, as shown in Table 19. The complementary hues differ slightly according to the value of *n*. If, on the other hand, the

TABLE 19.—RETARDATIONS AND RESULTING POLARIZATION COLORS FOR
DAYLIGHT ILLUMINATION

Retardation, mμ (1 mμ = 10 Å)	Color eliminated	Resulting polarization color	Order
0	. . . .	Black	
200	. . . .	Gray	
		White	
350	. . . .	Yellow	First
	Blue		
450	. . . .	Orange	
500	. . . .	Red	
550	Yellow	Violet	
650	. . . .	Blue	
700	Red	Green	
800	Violet	Yellow-green	Second
900	Blue	Yellow	
1,000	. . . .	Orange	
1,100	Yellow	Dark bluish red	
1,200	Violet	Blue-green	
1,300	. . . .	Green	
	Blue		
1,400	Red	Yellow-green	Third
1,500	. . . .	Purplish red	
1,600	Violet	Purple	
1,700	. . . .	Tinted grays of high order	

phase difference is one-half wave length or a fractional multiple of wave lenght, no interference will take place (see Fig. 235).

From the foregoing considerations, it is seen that the interference tint or polarization color produced by a given crystal is a function of the retardation or lag of the slow ray behind the fast ray. This retardation is obviously governed by the thickness and birefringence of the crystal, $\epsilon - \omega$, and not so obviously by the orientation of the crystal. The latter factor is more readily understood by referring back to Sec. 169 and Fig. 231, whence it appears that the apparent value of ϵ becomes smaller as the optic axis of the crystal is turned in the direction shown. The apparent birefringence becomes zero when the optic axis coincides with the direction of propagation of the entering light, *i.e.*, when the optic axis is vertical on the stage of the microscope.

(The term birefringence, of course, refers to the maximum birefringence.)

A useful equation correlates the factors of thickness and orientation of the crystal, mentioned above, and may be used for estimating either apparent birefringence or thickness

$$R = T(\epsilon - \omega)$$

where R = retardation, mμ.

T = thickness, mμ ($= 10^{-6}$ mm.).

171. Determination of Sign.—It is obvious that if we increase the thickness of a crystal that shows, say, a first-order yellow interference color, the retardation will thereby increase and the interference color will rise to red, blue, or green, etc., as the thickness of the crystal is progressively increased. In the same way, if we superpose a crystal giving, say, a first-order red tint and a crystal giving first-order gray so that their slow ray vibrations are parallel, then the resulting interference color will be of higher

Fig. 235.

order, *viz.*, blue. Thus reinforcement or "addition" of interference colors indicates similar orientation of the two slow rays

Fig. 236.—A typical form of compensator.

(and therefore of the two fast rays also). Similarly, if the slow ray of one crystal is vibrating at right angles to the slow ray of the other, then the retardations will cancel each other or "subtract," with an attendant decrease in the order of the resulting interference color.

The foregoing discussion leads logically to the conclusion that if we have a crystal plate ("compensator") upon which the direction of vibration of the slow ray is marked (Fig. 236) then, by superposing this plate on an unknown crystal, we can deter-

mine from the change in interference colors the direction of vibration of the slow ray in the unknown crystal. It has already been stated, however, that the extraordinary ray vibrates in the plane of the optic axis and that the optic axis is always the *c* axis in uniaxial crystals. Therefore, if we find that when the *c* axis of the unknown crystal is placed parallel to the slow ray of the compensator, reinforcement of the interference colors occurs, then the *c* axis must be the vibration direction of the slow ray in the crystal. Since the extraordinary ray vibrates in the plane of the *c* axis, the extraordinary ray of the crystal must be the slow ray, and the crystal is therefore positive.

In tabular form, the reasoning would be as follows:

1. When the slow ray of the compensator is parallel to the *c* axis of the crystal, the interference color rises. (Observed.)

2. Rise in interference color indicates that slow rays are parallel; hence the *c* axis must be the vibration direction of the slow ray.

3. But the extraordinary ray vibrates in the plane of the optic axis, or *c* axis by definition; hence the extraordinary ray must be the slow ray of the crystal.

4. If the extraordinary ray is the slow ray, then ϵ must be larger than ω, since refractive index varies inversely with velocity.

5. If ϵ is larger than ω, then $\epsilon - \omega$ is positive; hence, by definition of sign, the crystal is positive.

Note that this method of determining the sign is useless unless the crystal is sufficiently well defined so that the *c* axis is recognizable. In case the *c* axis is not recognizable, the longest direction of the crystal is chosen. If the slow ray vibrates lengthwise of the crystal, the *sign of elongation*, so-called, is positive. With few exceptions, the sign of elongation of uniaxial crystals is the same as the optic sign.

Several types of compensators are available. The mica quarter-wave plate which shows first-order gray is used for observations of crystals showing low birefringence. A selenite (gypsum) plate is more generally applicable. This compensator gives the "sensitive tint" of first-order red. A more elaborate device is the quartz-wedge, or combination-wedge, compensator which gives in succession all tints up to the third order or higher. Other devices for estimating birefringence are described by Johannsen.[8]

Experimental.—1. To illustrate the effect of birefringence on polarization color, examine slides of the following crystals, or

fragments which should be of comparable thickness.   Look up the refractive indices in each case: $NaClO_3$, NH_4ClO_4, SiO_2, $CaSO_4$, $NaNO_3$, $CsNO_3$.

2. To illustrate the effect of orientation on polarization color, observe a piece of mica under a very low-power objective or with no objective.   Tilt the mica with the fingers.   Study a slide of sodium nitrate prepared by fusion.   The thin, shapeless (anhedral) crystals are oriented at random, but all are of the same thickness.   Try cleaving the mica into thinner plates, and observe the change in color.

3. Place the selenite compensator on the stage, and rotate until the vibration direction of the slow ray (marked on the frame) is northwest by southeast.   Note the color of the field. Place the mica compensator in the slot provided, observing that its slow ray is northeast by southwest and that subtraction should therefore result.   Note the color of the field, then rotate the stage 90°.   Note the change to a higher order color, indicating that the slow ray vibration directions are now parallel.

4. Place a slide of salicin, nitroguanidine, or acenaphthene on the stage.   Rotate until some one crystal is in the 45° position (northwest by southeast or northeast by southwest).   Using crossed Nicols, observe the polarization color, if any.   Place a mica compensator in the slot provided.   Observe the color of the field and the color of the crystal.   Is the crystal of higher or lower order than before?   Is it higher or lower than the color of the field?   Rotate the crystal to the other 45° position, *i.e.*, 90° from the original direction.   Again note the colors.   Repeat, using other crystals on the same slide, then use the selenite plate, and then the quartz wedge.   The foregoing procedure should be employed in every case.   Use of only one compensator frequently leads to erroneous results.

5. Choose a crystal with tapering edges that show concentric color halos.   Align the crystal in a 45° position, introduce the quartz·wedge slowly, and note whether the color halos move toward or away from the thin edges.   Turn the stage 90°, and repeat.   If the colors move toward the thin edges, does this indicate addition or subtraction?

6. Determine the birefringence of a thin crystal of acenaphthene or of a piece of cellophane by the following procedure (after Johannsen[8]): Place the crystal in the 45° position, or 45°

from extinction. Insert the quartz wedge, and note the color changes. If subtraction is not observed, rotate the stage 90°. Insert the compensator until compensation occurs, being marked by the appearance of a black bar across the crystal. Remove the slide from the stage, but do not disturb the compensator. The center of the field should now show the original color of the crystal. Observe this color closely, then withdraw the wedge slowly, counting the number of times the field becomes red, *i.e.*, determine the order of the color. Obtain the retardation value from Table 18. By measuring the thickness of the crystal (see Chap. IV), calculate the birefringence, or, if the birefringence is known, calculate the thickness.

172. Pleochroism.—When a uniaxial crystal is placed on the stage so that the optic axis is horizontal and coincident with the vibration plane of the polarizer, then, as we have seen, the crystal transmits only the extraordinary ray. Similarly, if the optic axis is horizontal and at right angles to the vibration direction of the polarizer, then only the ordinary ray is transmitted. If the crystal shows a difference in the velocity at which it transmits light in these positions, it is called anisotropic, but if it also shows a difference in the *degree of absorption* of light (analyzer out), it is called *dichroic*, or, more generally, *pleochroic*. Thus, a dichroic crystal might be opaque to the ordinary ray and transparent to the extraordinary ray, or vice versa. More frequently the difference exhibits itself as a variation in hue, one ray appearing, perhaps, yellow and the other red. (This fact would be denoted by the "pleochroism formula," *e.g.*, ϵ = red, ω = yellow.)

In uniaxial crystals, the optic axis and the normal thereto are the directions of maximum or minimum absorption, or *absorption axes*, and, as one would expect, a section of a pleochroic substance shows no pleochroism when viewed along the optic axis.

In view of the fact that the optical properties of biaxial crystals have not yet been treated in detail, it may only be said at this point that there may be three absorption axes and three possible pleochroic colors (trichroic). In the orthorhombic system, the crystal axes and absorption axes coincide; in the monoclinic system, only the *b* axis coincides with an absorption axis; and in the triclinic system, there is no necessary relation between the two sets of axes. (Compare character of extinction, Sec. 167.)

CHAPTER VI

IDENTIFICATION OF CRYSTALS WITH THE POLARIZING MICROSCOPE

154. It is apparent from the preceding chapter that identification of crystalline substances by their outward or geometrical characteristics, such as class, habit, and interfacial angles, is not an altogether easy matter. Also, the relatively large specimens of well-developed crystals necessary for the study are not always obtainable. However, the identification of crystalline materials by means of their optical properties is fairly easy to carry out and requires only a few milligrams of sample, which may even be in the form of a powder (particles > 0.05 mm.).

OPTICAL PROPERTIES OF ISOTROPIC MATERIALS

155. In order to provide a foundation for the discussion that follows, it is necessary to review a few fundamentals and definitions from elementary optics.

1. Light is a form of energy which for the present purpose is considered as transverse waves or vibrations traveling at about 186,000 miles/sec. in a vacuum. The wave length of the vibration determines the color of the light.

2. The velocity of light in a transparent substance is characteristic of the substance and is less than the velocity in a vacuum. Further, the velocity of light in any substance is dependent on the wave length of the light, the velocity of red light being greatest.

3. The refractive index of a substance is the ratio of the velocity of monochromatic light in a vacuum to the velocity in the substance

$$n = \frac{v \text{ (in vacuum)}}{v \text{ (in substance)}}$$

4. Owing to this difference in velocity, a ray of light is bent when it passes obliquely from one medium into a second medium of different refractive index. The fundamental equation

expressing this fact is

$$n = \frac{\sin i}{\sin r}$$

where i is the angle of incidence and r is the angle of refraction, both angles being measured from the normal to the boundary between the two media. It follows from paragraph 2 that the refractive index is a function of the wave length or the color of the light; short waves are bent most, and a substance shows its highest refractive index for violet light, its lowest refractive index for red light.

5. An isotropic substance is a substance that has only one refractive index, *i.e.*, it transmits light with equal velocity in all directions. Isotropic substances include gases, liquids, glasses, and crystals of the isometric system, *e.g.*, NaCl or KI.

156. Measurement of the Refractive Index of Solid Isotropic Substances.—If powdered glass ($n = 1.5$) is suspended in water ($n = 1.3$), the outlines of the grains are easily seen because the illuminating light is bent or refracted and scattered as it passes from the water into the glass. If, however, the powdered glass is suspended in a medium that has exactly the same refractive index as the glass, the light will not be bent in passing from one medium to the other, the suspension will be optically homogenous, and the particles will be invisible (see Fig. 208).

$n_1 \neq n_2$ $n_1 = n_2$

Fig. 208.

The obvious conclusion which may be drawn from this experimental fact is that in order to measure the refractive index of a powdered isotropic substance, it is necessary to suspend the sample in a series of liquid media of known refractive index, until a medium is found in which the particles become invisible. The procedure may be carried out on a series of microscope slides, in the following manner:

Experimental.—The sample is crushed in an agate mortar, or, if friable, upon a microscope slide. A few grains are sprinkled over a small area on a clean slide and are covered with a ⅜- to ½-in. cover glass. A drop of mounting medium, adhering to a

glass rod, is brought in contact with the slide a short distance from the edge of the cover glass so that it flows under the latter by capillary attraction.   The immersed grains are then examined under the microscope.   The long-focus condenser used should be stopped down and lowered so as to give a narrow, almost parallel pencil of light.   Use a yellow filter.   Examine powdered glass ($n = 1.515$) in media 1.510, 1.520, 1.515, or sodium chloride ($n = 1.544$) in media 1.540, 1.550, 1.545.   Either the 16- or the 4-mm. objective may be used.   (Save the slides for the next two experiments.)

157. The Becke Line.—When a crystalline fragment shaped roughly like a convex lens is immersed in a liquid of *lower* refrac-

Objective

Coverglass
Liquid

$n_{particle} > n_{medium}$ $n_{particle} = n_{medium}$ $n_{particle} < n_{medium}$
FIG. 209.

tive index, the fragment tends to converge light, as does a convex glass lens in air.   When such a particle is illuminated by a narrow beam of parallel light and observed under the microscope, it appears to be surrounded by a bright fringe, or "halo," known as the Becke line.   When the microscope is focused upward by raising the tube, the halo appears to move inward toward what may be called the focal point of the lens particle.   If the refractive index of the particle is less than that of the medium, the particle acts as a diverging lens and the Becke line moves outward as the objective is raised.   This phenomenon is illustrated in Fig. 209.   The Becke line is shown not only by fragments of the type illustrated, but also by crystals with vertical edges, *e.g.*, NaCl (Fig. 210), and by spheroidal droplets such as oil globules or bubbles.   The optical theory of the former case has been the subject of some misunderstanding.   The correct explanation is given by Saylor.[1]   The utility of the Becke line as a guide to the determination of refractive index by the immersion method

is summed up in the following rule: On raising the focus of the microscope, the Becke line moves toward the medium of the higher refractive index.

Experimental.—Reexamine the slides of powdered glass or sodium chloride mentioned above, and observe the movement of the Becke line.   The $10\times$ objective and low-power condenser should be used.   The condenser is lowered and the iris stopped

Fig. 210.—Appearance of NaCl ($n = 1.544$) in medium 1.540.

down to give a narrow cone of rays approximately focused on the object.   Try the $45\times$ objective also.   The habitual use of a yellow filter is recommended.   Use of a sodium-vapor lamp gives even better results.

158. The Half-shadow Method.—A similar method of discovering whether the refractive index is higher or lower than that of the surrounding medium is provided by shading half the field

Fig. 211.—The half-shadow test.

of view of the microscope and noting which side of the particle is shaded.   (Use white light.)   If the particle is shaded on the same side as the microscope field, then the particle has the higher index.   Conversely, if the shading is on the opposite side, the particle has a lower index than the medium (Fig. 211).   The shadow is customarily produced by inserting a card below the substage so that about four-fifths of the objective aperture is darkened.   Alternatively, if the microscope is provided with a

sliding analyser or a body-tube slot for a compensator, the analyser or compensator may be pushed halfway in to darken part of the field.   Whatever the means used to shadow the field, it is necessary that the particle be at or above the focal point of the condenser, or the effects will be reversed.[1]   The condenser should be lowered, and a low-power objective should be used. Under ideal conditions, it is possible to measure refractive indices to ±0.0005 by the Becke and half-shadow methods, although in practice the error may be as much as ±0.002.

When the index of the particle is fairly close to that of the medium, the shadings observed in the particle may be colored. The appearance of a light blue border on the "bright" side and a

Fɪɢ. 212.—Explanation of the half-shadow test.

pale red or brown border on the shadow side indicates that the refractive index of the particle and the medium are the same for yellow light.   An accuracy of roughly ±0.001 may be achieved by this test under usual conditions, provided that the dispersion of the liquid is not too great.

The theory underlying the appearance of the tints is simple and involves two facts: (1) that the dispersions of liquids is generally greater than that of solids, and (2) that the refractive index of any substance is greater for blue than for red light.   Thus in the preceding case, if the refractive index of the fragment is equal to that of the medium for yellow light, then the medium will have the larger index for blue light and the smaller index for red light. If the particle were illuminated with red light, it would be shaded on the same side as the field, whereas if illuminated with blue

light, it would be shaded on the opposite side.   When illuminated with white light, which is composed of all colors, the fragment will appear bluish at one edge and red at the other.   Since the phenomenon depends on the relative dispersive powers of the fragment and the immersion medium, it is not always observable.

The observation that the Becke line disappears as the substage diaphragm is opened was put to good use by Viola,[8] who worked out the relation

$$n_1 = kD^2 - n_2$$

where n, and n_2 are the indices of particle and medium (or vice

versa), D is the diameter of the diaphragm opening (in millimeters), which will just cause the Becke line to disappear, and k is an experimentally determined constant for the microscope.

Experimental.—Examine powdered glass in prepared mixtures of neutral oil and α-bromonaphthalene: $n = 1.510, n = 1.515$, and $n = 1.520$.   Note the half-shadow tints and the relative positions.   Try the Becke test also.

159. Determination of the Refractive Index of Liquids.—It might be noted here that the preceding tests apply to liquids in capillary tubes as well as to solid fragments.

Fig. 213.—Simple schlieren cell.

The so-called schlieren test[2,3,4] depends on the same principle as the half-shadow method and is carried out as follows:

A specially prepared flat-walled cell is used, which may be constructed from ordinary microscope slides and Lucite (Fig. 213).   The microscope is placed in a horizontal position and adjusted for oblique illumination as above.   The cell, containing a liquid of known refractive index, is fastened to the stage, and a tiny capillary pipette, containing the liquid of unknown index, is introduced into the cell so that its tip is below the surface of the medium.   As the unknown liquid slowly flows into the medium, a striation or schlieren current forms.   This is observed through the microscope, and the shading is noted as for the half-shadow test on solids.   A microscope equipped with special half-shadow diaphragms is used for more precise determinations

(see Saylor[1]).   By this means, the refractive index of exceedingly minute samples may be determined to approximately ± 0.0005. The method is also applicable to density determinations, since the schlieren current will move either up or down, depending on whether the added liquid is lighter or heavier than the medium of known density.

Emich[2] cites the utility of the method for determining the concentration of a solution by observing a series of schlieren in prepared solutions of known concentration.   It may also be used for determining the purity of a liquid, either by comparison with a known sample or with a distillate of the suspected liquid, conveniently obtained by microdistillation in an Emich tube.[2]

160. The Double-variation Method.—This method of determining the index of refraction is exactly the same in principle as the simple Becke method, but it gives additional information and is capable of greater accuracy.   The distinguishing feature lies in the use of comparatively few immersion media, whose refractive indices are varied by changing the temperature and the wave length of the monochromatic illumination used (see tables in Winchell[6]).

In practice, a special hollow slide is employed, whose temperature is maintained at any desired level by a stream of warm water, which is also conducted through the hollow prism casing of an Abbe refractometer (Sec. 201).   The source of illumination for both microscope and refractometer is a monochromator of high intensity.   The fragment of unknown material is placed on the slide and mounted in some liquid of nearly the same refractive index.   A drop of the same liquid is placed in the refractometer.   While maintaining a given temperature, the wave length is adjusted until the Becke line of the particle disappears, when the index of the mounting liquid is read from the refractometer.

Several such match points are determined at various wave lengths by changing the temperature, so that the dispersion curve of the particle may be plotted (n vs. λ) (see Fig. 214).   The index of refraction n_D for the sodium line (5,893 A) may be read from this curve and also the dispersion $n_F - n_C$ or $n_{Tl} - n_{Li}$ where F and C refer to the blue and red lines of the hydrogen spectrum (4,861 A, 6,563 A) and Tl and Li refer to the thallium and lithium lines (5,351 A, 6,708 A).   It is assumed that the index

of the solid does not change appreciably with temperature. The dispersion, incidentally, is a characteristic constant which is of diagnostic value.

Owing to the expense of the necessary equipment, the refined method described above is not likely to become popular as such. It is possible, however, to economize, with some sacrifice of accuracy, by dispensing with both monochromator and refractometer. The monochromatic light may be supplied by a mercury arc or incandescent lamp used with suitable filters, and according to Emmons,[5,6] the n vs. T and n vs. λ curves for the

Fig. 214.—Typical data from the double-variation method. The curve $ABCD$ shows the relation of the refractive index n of a particle to the wave length λ. From this curve the refractive index at the standard wave length 589 $m\mu$ may be obtained, as well as the standard dispersion $n_{487} - n_{656}$.

various media used may be plotted once and for all when the liquids are made up. These media are for the most part pure liquids whose properties do not vary over long periods of time.

161. Experimental.—Referring to the table of refractive indices at the end of the chapter identify an isotropic crystal by the following procedure:

Crush the material, and place a few milligrams in a small, approximately 100-mesh sieve. (The small sieves used to filter tap water serve very well.) Tap the sieve so that a half dozen grains fall in a small area on a microscope slide. Place a ½-in. cover glass over the particles, introduce a drop of immersion medium, and examine under the microscope. Note the relief or distinctness of the particles. If they stand out clearly, appear dark, opaque, or rough, their index is probably considerably

different from that of the medium.   Using the Becke test as a
guide, make up another slide in a different medium.   Repeat
the process until the Becke and half-shadow tests show that the
indices are within 0.005.   By taking the next higher or lower
medium, it is possible to estimate the index to about 0.002.   In
precise work, it is advisable to check the index of the final medium
with a refractometer.   After some experience, it should not be
necessary to make more than three or four trial slides.

162. Immersion Media.—The series of liquids used for deter-
mining the refractive index of particles by the simple immersion
method has been the subject of considerable research, since the
accuracy of a determination depends largely on the medium used.
The properties of an ideal series are discussed by Buerger.[7]

In the following paragraphs, some of the usual mixtures are
described.   For a more comprehensive summary, see Johannsen[8]
and Chamot and Mason,[9] who list media up to $n = 2.70$.

TABLE 14.—MIXTURES USED AS IMMERSION MEDIA

Range	Components	Reference
1 355–1.460	Petroleum distillates	2, 7
1 411–1.466	Government oil and *n*-decane	6
1.429–1.456	Petroleum distillates	3
1.384–1.498	Ethyl propionate and mesitylene	4
1.423–1.658	Heptylic acid and α-bromonaphthalene	4
1.493–1.658	*n*-Butylphthalate and α-bromonaphthalene	4
1.460–1.632	Kerosene and α-chloronaphthalene*	7
1.633–1.658	α-Chloronaphthalene and α-bromonaphthalene	
1.633–1.739	α-Chloronaphthalene and methylene iodide	6
1.739–1.780	Methylene iodide and sulfur	6
1.780–1.800	Above plus tetraiodoethylene	
1.800–1.843	Above plus phenyldiiodoarsine	5
1.780–1.960	Methylene iodide, sulfur, and sulfides	9

* Commercial Halowax is suitable.

The media listed in Table 14 are designed primarily for use in
determinations of inorganic materials and may be unsuitable for
determining the refractive index of organic compounds which are
soluble in many of the liquids.   Several series of aqueous mixtures
have been devised for the latter purpose, as well as mixtures of
oils having low solvent power.

Glycerol may be advantageously substituted for water in the
last three mixtures in Table 15, since it reduces the volatility.

This advantage is offset by its hygroscopic property, which, however, is serious only in humid atmospheres.

In making up any one of the sets of media given in Table 14 and Table 15, it is advisable to use 15-ml. brown-glass bottles with ground-in droppers and ground-glass caps. Some mark should be made on the label to indicate the components of the mixture. The bottles are conveniently kept in a wooden block drilled with holes of suitable size, and the set should be kept in a lighttight box or drawer.

TABLE 15.—AQUEOUS IMMERSION MEDIA

Range	Components	Reference
1.335–1.400	Water, glycol, glycerol	12
–1.610	Water, glycerol, zinc iodide	
–1.700	Water, cadmium borotungstate	8
–1.720	Water, potassium mercuric iodide	8
–1.793	Water, barium mercuric iodide	8

The lower nonaqueous media are prepared by fractionally distilling petroleum ether, through a packed column, and blending adjacent fractions to the desired index. These media are very volatile, but their index does not change on evaporation. For liquids above $n = 1.430$, the simpler procedure of Bosazza[10] is recommended. Kerosene (flash point = 300°F.), which is free from objectionable odor, is distilled in a tall-necked distilling flask, and the desired fractions are collected.

So-called "government oil" is a petroleum fraction that is quite pure and nonvolatile. It is blended with α-chloronaphthalene (trade name Halowax) according to the mixing curve given by Kaiser and Parrish.[11] These authors also give mixing curves for α-chloronaphthalene and methylene iodide and for methylene iodide and sulfur.

The equation $n(V_1 + V_2) = n_1V_1 + n_2V_2$ serves as a rough guide to the preparation of binary mixtures of index n, from volumes V_1 and V_2 of the end members whose indices are n_1 and n_2, respectively. The indices are read from an Abbe or other refractometer and should be within ± 0.0005 of the index recorded on the bottle. For methods of measuring high refractive indices, see Chap. VII.

TABLE 16 —REFRACTIVE INDEX MEDIA*

	N_D 20°C
Methyl alcohol	1 3288
Water	1 3330
Acetone	1 3592
Lthyl acetate	1 3727
n-Hexane	1 3755
n-Heptane	1 3872
n-Butyl alcohol	1 3991
n-Butyl chloride	1 4022
1, 4-Dioxane	1 4223
Methyl cyclohexane	1 4235
Ethylene glycol	1 4318
Lthyl citrate	1 4434
Ethylene chloride	1 4453
Trimethylene chloride	1 4476
Cyclohexanone	1 4507
Cyclohexanol	1 4678
Diethanolamine	1 4782
Triethanolamine	1 4853
p-Cymene	1 4908
s-Tetrachloroethane	1 4943
Toluene	1 4957
Benzene	1 5017
Ethyl iodide	1 5138
Anisole	1 5178
Trimethylene bromide	1 5238
Chlorobenzene	1 5250
Methyl iodide	1 5310
Ethylene bromide	1 5383
o-Nitrotoluene	1 5466
Nitrobenzene	1 5526
Tri-o-cresyl phosphate	1 5582
Bromobenzene	1 5602
o-Toluidine	1 5725
Aniline	1 5864
Bromoform	1 5973
o-Iodotoluene	1 6095
Quinaldine	1 6120
Iodobenzene	1 6205
Quinoline	1 6272
s-Tetrabromoethane	1 6378
α-Bromonaphthalene	1 6585
Methylene iodide	1 74

* Sold in 25-ml bottles by the Eastman Kodak Company (indices as given).

ANISOTROPIC CRYSTALS

163. The foregoing discussion has been confined to isotropic substances which transmit light with equal facility in any direction. The great majority of crystalline materials, however, are anisotropic, or nonisotropic, and transmit a ray of light with varying velocity according to the direction of the ray in the crystal. Since the refractive index depends on the velocity of

Fig. 215a.—Unpolarized light.

Fig. 215b.—Polarized light.

light in the substance, it follows that the refractive index of an anisotropic crystal depends on the orientation of the crystal. Crystals may be classified according to the number of distinguishable and characteristic refractive indices that they exhibit.

Table 17.—Optical Classification of Crystals

Isotropic	Anisotropic	
	Uniaxial	Biaxial
One refractive index n..	Two refractive indices ω and ϵ	Three refractive indices α, β, and γ
Isometric crystals, liquids, and glasses.	Tetragonal, hexagonal, and r h o m b o h e d r a l crystals	Orthorhombic, monoclinic, and triclinic crystals

164. Polarization of Light by Anisotropic Crystals.—Before undertaking the study of anisotropic crystals, it is necessary to review the concept of polarization of light. An especially clear and simple discussion of polarized light is given by Robertson.[18] For the present purpose, it is sufficient to describe light as a wave motion whose waves or vibrations are normal to the direction of propagation and which are in a family of planes including the

direction of propagation.   A hypothetical view of a ray of light traveling perpendicular to the plane of the paper is shown in Fig. 215*a*.

FIG 216.

Plane polarized light is light whose vibrations have all been brought into one plane, as shown diagrammatically in Fig. 215*b*.

Plane polarized light may be produced in several ways:

1. By partial reflection, as from a sheet of glass or polished desk top, also by reflection (scattering) from colloidal particles.

2. By means of the Nicol prism and related devices.

3. By means of pleochroic anisotropic crystals, *e.g.*, tourmaline and iodo-quinine sulfate. (*Polaroid* consists of tiny, needle-like crystals of the latter substance mounted in a plastic base which is then stretched or otherwise processed so that the crystals are lined up with their long directions substantially parallel.)

FIG. 217.

When unpolarized light enters a uniaxial crystal, *e.g.*, calcite ($CaCO_3$, rhombohedral), the various layers of ions in the crystal lattice somehow *resolve* the heterogenous light vibrations into two mutually perpendicular planes.   Note that the process is one of resolution and that no rays are filtered out.   Figures 216 and 217 show how one of the random light vibrations AA' is resolved on entry into a crystal into its components OO' and EE'.

The resolution takes place at the moment of entry into the crystal, and the net effect is the production of two polarized rays, vibrating in mutually perpendicular planes. These two rays then proceed through the crystal with unequal velocities, and hence the crystal exhibits two refractive indices, a low refractive index for the faster ray, a high refractive index for the slower ray. One of these rays vibrates in a plane which includes the direction of propagation of the ray and the *c* axis of the crystal, and since this ray exhibits anomalous behavior, it is known as the *extraor-*

FIG. 218.   FIG. 219.—The Nicol prism.

dinary ray. The other, the *ordinary* ray obeys the usual laws of refraction and vibrates in a plane including the direction of propagation and perpendicular to the plane of the *c* axis.

Since the refractive index of the crystal is less for one ray than for the other, the two rays will proceed along different directions in the crystal after refraction at an inclined surface. This is illustrated in Fig. 218, which shows the passage of the two polarized rays through a rhombohedron of calcite.

165. The Nicol Prism.—In order to obtain a ray of pure polarized light, it is necessary to get rid of one of the two rays indicated in Fig. 218. This separation of a single ray is accomplished in the Nicol prism (Fig. 219) by total reflection of the

ordinary ray from a film of Canada balsam. The Nicol prism is constructed from a natural crystal of calcite by grinding the original rhomb faces to an acute angle of 68°. The rhomb is then cut in two, and the halves are cemented together again with Canada balsam. Balsam is chosen because its refractive index (1.54) is intermediate between the refractive index for the extraordinary ray (1.486) and the ordinary ray (1.658). Light enters the crystal as shown, and is resolved at once into the extraordinary ray (the fast ray in the case of calcite) and the slow, ordinary ray. These rays pursue different courses through the crystal and impinge on the Canada balsam layer. Here, the extraordinary ray goes from a medium of low refractive index into a medium of higher refractive index and is therefore refracted slightly toward the left (Fig. 219), whereas the ordinary ray passes from a medium of high refractive index into a medium of lower refractive index. The angles of the prism have been adjusted so that the ordinary ray strikes the balsam interface at an angle slightly greater than the critical angle and is therefore totally reflected out to the side. The extraordinary ray, however, traverses the balsam layer and the second portion of the prism, from which it emerges as plane polarized light vibrating in a plane that is parallel to the optic plane of the calcite. This plane includes the c axis of the crystal and the short diagonals of the end faces, as shown in Fig. 218.

FIG. 220.

If, now, this polarized light enters a second Nicol prism, (Fig. 220) several things can happen, depending on the relative orientation of the optic planes of the two prisms. If these optic planes are parallel, then the polarized light from the first prism, or polarizer, passes through the second prism, or analyzer, unchanged. If, however, the optic planes of the polarizer and the analyzer make an angle θ with one another, the original polarized ray will be resolved when it enters the second prism as shown diagrammatically in Fig. 221. The two resultants FF' and SS' in the analyzer A are the fast and slow rays discussed in the preceding paragraph. The slow, ordinary ray SS' is rejected at the balsam interface, whereas the fast, extraordinary ray FF' con-

tinues on through the prism.   The amplitude of the ray leaving the analyzer is given by the equation

$$\frac{A}{A_o} = \frac{FF'}{PP'} = PP' \cos \theta$$

where A and A_o represent the transmitted and original amplitudes (FF' and PP', Fig. 221).   Since intensity is proportional to the square of the amplitude, the equation may also be written as $I/I_o = \cos^2 \theta$ where I and I_o are the transmitted and original intensities.   Note that the polarizer P alone transmits just one-half of the entering light and that if $\theta = 90°$ the analyzer will reject all the light from the polarizer, when the two Nicols are said to be "crossed."

166. The polarizing microscope (Fig. 222) is a microscope equipped with a Nicol prism or Ahrens polarizer (Fig. 223), located below the condenser, and an analyzer that may be mounted in the body tube ("sliding analyzer") or placed on top of the eyepiece ("cap analyzer").   The sliding analyzer is usually of the Ahrens type and is fitted with compensating lenses.   Polaroid disks may be used instead of more expensive prisms, but their faint brownish color is objectionable for many purposes.   Whatever means of polarization is employed, the polarizer should be set in a graduated mounting which allows rotation.   In this text, it will be assumed that the optic plane or vibration plane of the polarizer is normally north-south and that the analyzer is crossed, i.e., its vibration plane is east-west.

Fig. 221.—PP' = vibration plane of light from the polarizer; AA' = optic plane (vibration plane) of analyzer; FF' and SS' = resultants formed in analyzer, of which only FF' is transmitted.

In addition to the polarizing apparatus, the polarizing microscope is usually fitted with a rotating graduated circular stage, a special Bertrand lens in the body tube, and an eyepiece that has accurately oriented north-south and east-west cross hairs in the focal plane of the eye lens.

The function of the Bertrand lens will be discussed in Sec. 173, but for the present purpose it may be considered as a means of focusing the ocular on the rear lens of the objective where interference figures (Sec. 173) are located.   It is a convenience rather

FIG. 222.—The polarizing microscope.   (*Courtesy of Spencer Lens Company.*)

than a necessity. Both the Bertrand lens and the sliding analyzer may be swung out of the body tube when they are not in use. Chamot and Mason[9] describe several standard polarizing microscopes in detail and give particulars as to their care and handling. West[20] gives several methods of converting an ordinary microscope to a polarizing microscope through use of Polaroid. All
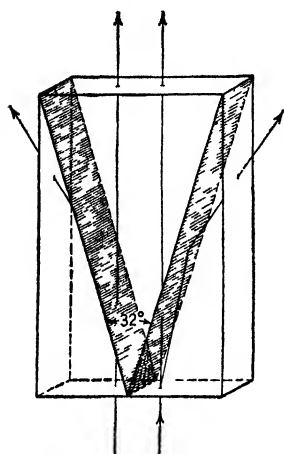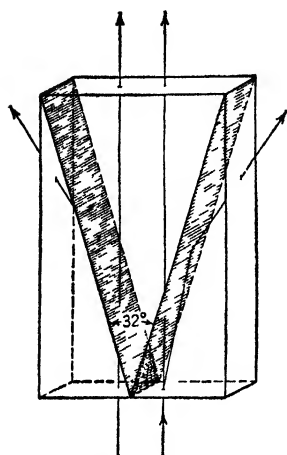
FIG. 223.—The Ahrens prism.

the information on microscopes given in Chap. IV applies to polarizing microscopes as well and should be reviewed at this point. It is especially important that the iris diaphragms, the condenser, the objective, and the ocular be perfectly aligned with the center of rotation of the stage.

167. Use of the Polarizing Microscope—Character of Extinction.—If an isometric crystal, say sodium chloride, is placed on the stage of a polarizing microscope and is examined between crossed Nicols, it is found that both the field of view and the crystal are completely dark. This is so because the internally symmetrical atomic lattice of an isotropic crystal has no effect on the polarized light from the polarizer no matter how the crystal is oriented. Isometric crystals are isotropic and show complete, or *isotropic extinction*.

If, however, a uniaxial crystal such as a pinacoidal, tetragonal, or hexagonal crystal is placed with the *c* axis horizontal on the stage of the polarizing microscope, it will be alternately dark and light, or colored, as the stage is rotated. Further, the crystal will be dark or at extinction when a prominent face or edge is parallel to the north-south or east-west cross hair of the ocular, *i.e.*, when the *c* axis is parallel to the vibration plane of the polarizer or analyzer. At oblique positions, the crystal will be light and usually colored.

The explanation of this phenomenon is easily understood if the behavior of the light in the crystal is considered, as discussed above in the case of calcite. In Fig. 224, a crystal is shown as it appears in the field of view of the microscope. The various

planes of polarization are indicated as vectors.   *P* represents the vibration plane* of the polarized light from the polarizer, whereas *E* and *O* represent the vibration planes of the two component rays formed in the crystal whose *c* axis is so denoted.   These two rays then proceed up through the objective to the analyzer, which resolves both rays into a resultant vibrating in the plane *A* of the optic axis of the analyzer.   This resultant passes through the analyzer to the eye, and the crystal therefore appears light against a black background.

If the crystal is rotated so that its *c* axis is parallel to the vibration plane of the polarizer, as in Fig. 225, then no component ray *O* can be formed in the crystal, as is obvious from the vectorial

FIG. 224.   FIG. 225.   FIG. 226.

considerations involved.   The *E* ray, however, is formed and continues on up to the analyzer, which rejects it since it has no component in the east-west vibration plane of the analyzer. Thus the crystal appears dark against a dark background.   The crystal is likewise "extinguished" when only the *O* ray comes through, as in Fig. 226.   In short, the crystal is at extinction when the *c* axis is north-south or east-west, whether the axis is horizontal on the stage or inclined thereto.   If the crystal has edges or faces parallel to the *c* axis, then it will be extinguished when such an edge or face is parallel to one of the cross hairs. This is referred to as *parallel extinction*.   A rhombohedral, pyramidal, or domal crystal, on the other hand, will be extinguished when the bisector of a silhouette angle is parallel to a cross hair as shown in Fig. 227.   Such extinction is called

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* The term *vibration plane* indicates a plane including the direction of propagation of the ray and the *vibration direction* of the ray in the crystal. The vibration direction is normal to the direction of propagation and in the plane of an optic direction, which may be either the optic axis or a normal thereto.

symmetrical extinction.   Note that the bisector of the silhouette angle is in the plane of the *c* axis irrespective of any distortion of the ideal form of the crystal such as growth parallel to a face, as indicated by the dotted lines in Fig. 227.

Consider now a uniaxial crystal resting on the stage with the *c* axis vertical.   Since the *c* axis of a uniaxial crystal is the axis of maximum symmetry, the atomic lattice of the crystal as viewed along the *c* direction shows symmetry comparable to that of the atomic lattice of a cubic crystal.   On this basis, it is not surprising to find that a uni-axial crystal affects light traveling in the *c* direction much as does an isotropic crystal, *i.e.*, the light from the polarizer passes through the crystal effectively un-changed.   Since the trans-mitted ray is "crossed" with respect to the analyzer, the crystal shows complete or *isotropic extinction*.   The crystal is dark no matter how the stage is turned.   The direction of the *c* axis of a uni-axial crystal is called the *optic axis* and may be defined for the present purpose as that direction along which a ray of light may travel without the formation of an extraordinary ray.   Note that the optic axis is a direction or family of parallel lines, and not a single line.   Since no extraordinary ray is formed, a crystal oriented with its optic axis vertical on the stage shows only the refractive index ω characteristic of the ordinary ray.

Symmetrical Extinction
FIG. 227

Table 18 which lists extinction characters includes biaxial crystals as well as uniaxials, thereby anticipating any theoretical discussion of biaxials.   It will be sufficient for present purposes to regard biaxial crystals as similar to uniaxial crystals, with the exception that in the monoclinic and triclinic systems the vibra-tion planes may be inclined to the crystallographic axes, *i.e.*, the optic directions need not be parallel to faces or to the bisectors of face angles.   Since a crystal is extinguished when the vibration direction is north-south or east-west, the faces or edges of the

extinguished monoclinic or triclinic crystal need not be parallel to the cross hairs. If the prominent faces or edges of an extinguished crystal make an angle with the cross hairs, the extinction is said to be oblique (Fig. 228). (Compare with symmetrical extinction; avoid confusing the two.)

Fig. 228.—Types of extinction.

In the monoclinic system, there is some correspondence between vibration directions and crystallographic axes in that the *b* (ortho) axis, which is the single axis of symmetry, is always a vibration direction. For this reason, the monoclinic crystal shows parallel extinction when the *b* axis is horizontal and oblique extinction when the *b* axis is not horizontal. In the triclinic system, there is no necessary correspondence between vibration directions and crystallographic axes.

The angle between a prominent face of an extinguished crystal

Extinction angle
Fig. 229.

and the nearest cross hair is called the extinction angle (see Fig. 229). Note that this is always less than 45°. It is advisable to measure extinction angles to several faces, and, further, to check the possibility of symmetrical extinction, it is best to measure the profile angles also. Then if the extinction angle is found to be half the profile angle, the extinction must be symmetrical. Conventionally, the maximum extinction angle is the one recorded for purposes of identification or reference.

Two devices are commonly used for exact measurement of extinction angles: the selenite compensator and the Bravais

TABLE 18.—DIFFERENTIATION OF CRYSTAL SYSTEMS BY CHARACTER OF
EXTINCTION

System	Extinction
Isometric............	Isotropic or complete
Tetragonal..........	Parallel or symmetrical. Some isotropic. Latter usually have four-sided silhouette
Hexagonal...........	Parallel or symmetrical. Some isotropic. Latter usually have three- or six-sided silhouette
Rhombohedral........	Symmetrical. Few isotropic. Latter usually are three-sided
Orthorhombic........	All show parallel or symmetrical extinction
Monoclinic	Some parallel or symmetrical, some oblique
Triclinic.............	All oblique

twinned mica plate (Fig. 230).   The former, described in Sec. 171,
is inserted in a slot above the objective.   The crystal is viewed

FIG. 230.—The Bravais
plate. (Direction of
lines indicates vibration
planes.)

through this plate, and when at extinction,
the color of the crystal exactly matches
that of the plate.   The Bravais plate and
similar devices are described by Johannsen.[8]
These plates are composed of two or more
crystal sections mounted in a frame that
fits the compensator slot or a slot in the
ocular.   A crystal at extinction appears
the same color in each part of the field, and
rotation of as little as 0.3° causes a
perceptible change in the color of the two
halves.

The determination of system by extinction depends on two
assumptions: (1) that many well-formed crystals are involved,
and (2) that the crystals are oriented at random, *i.e.*, not all
lying on one face.

Experimental.—Examine prepared slides of acenaphthene
(orthorhombic), nitroguanidine (tetragonal), copper sulfate
pentahydrate (triclinic), potassium chlorate (monoclinic) (note
possibility of confusing oblique and symmetrical extinction),
lead iodide (hexagonal), sodium nitrate (rhombohedral), ammo-
nium or potassium dihydrogen phosphate (tetragonal), potassium
persulfate (triclinic), silver nitrate (orthorhombic), sodium

nitrate (rhombohedral), sodium chlorate (isometric) potassium alum (isometric), and oxalic acid dihydrate (monoclinic).

Determine the character of extinction of an unknown crystal. Sprinkle crystals onto a thin film of tacky Canada balsam or glycerin jelly to ensure random orientation. Examine only the more perfect specimens. If the extinction is oblique, measure the extinction angle for at least a dozen crystals, using the vernier of the rotating stage.

168. The Measurement of Refractive Indices of Uniaxial Crystals.—By referring back to Figs. 225 and 226, it is seen that when a crystal is at extinction only one polarized ray emerges from the crystal and proceeds up to the analyzer, which rejects it. If the analyzer were removed, however, this single ray would continue up to the eye and a light image of the crystal would be seen against a light background. Because of the fact that only one ray emerges from the crystal, however, the crystal will show only one refractive index. If the optic axis of the crystal is horizontal and north-south, then the E vibration or extraordinary ray (Fig. 225) comes through the crystal which therefore shows the refractive index ϵ characteristic of the extraordinary ray. This refractive index can be measured by the immersion methods.

Conversely, if the crystal is oriented with the c axis east-west, as in Fig. 226, then only the ordinary ray comes through the crystal, which then exhibits the refractive index ω characteristic of the ordinary ray. Thus, the method of determining the two refractive indices of a uniaxial crystal is just the same as for isotropic crystals, with the sole difference that in the case of the uniaxial crystal it is first necessary to align the crystal in the proper position.

Experimental.—Nitroguanidine is uniaxial and is elongated along the c axis. Using a slide of nitroguanidine crystals mounted in Canada balsam, place a needle north-south at extinction, *i.e.*, parallel to the vibration plane of the polarizer. Remove the analyzer, and note the movement of the Becke line. Rotate to the east-west position, and again note the movement of the Becke line. Which is larger, ϵ or ω? Does the slow ray vibrate lengthwise or crosswise of the crystal?

Determine the two refractive indices of nitroguanidine or some other acicular uniaxial crystal, such as urea, by the foregoing procedure through the use of suitable immersion media.

169. Note that ϵ (extraordinary ray) may be measured only on crystals whose optic axes are horizontal on the slide and oriented parallel to the north-south vibration plane of the polarizer. If the optic axis is not horizontal, then ϵ cannot be measured. The refractive index obtained if the optic axis were tilted in the *north-south plane* would be intermediate between ϵ and ω, and its magnitude would be a function of the degree of inclination of the optic axis. As the optic axis becomes more nearly horizontal, the observed refractive index approaches ϵ as a limit, and as the

Fig. 231.—Uniaxial index ellipsoid ($+$).

optic axis becomes nearly vertical, the observed index approaches ω. Similarly, ω is observable only when the optic normal is horizontal.

The relation between the orientation of a crystal and the observable refractive index is conveniently summarized in the so-called *index ellipsoid* shown in Figs. 231 and 232. This is an ellipsoid of revolution about axis AC, which is the vibration direction of the extraordinary ray. The magnitude of the refractive index ϵ for the extraordinary ray is represented by the semi-axis AB. The length of the semi-axis BG corresponds to the magnitude of the refractive index ω. Note that BG is a radius of the circular section.

In order to find the relation between the orientation of a crystal and its observable refractive indices, it is customary to visualize such an ellipsoid within a crystal whose c axis corresponds to AC. If the light from the polarizer enters the crystal along the FD

axis of the ellipsoid, it is broken up as we have seen into an extraordinary ray, vibrating in the direction AC, and an ordinary ray, vibrating in the direction GH. The length AB gives the magnitude of the extraordinary ray index ϵ, whereas the index ω, for the ordinary ray, corresponds to the length of the other semi-axis $BG = BD = BH = BF$. Thus, if light travels normal to

FIG. 232.—Uniaxial index ellipsoid ($-$).

the optic axis, both ϵ and ω may be determined. If the optic axis is tilted so that the entering light travels along some direction such as JB, it is resolved, as before, into two rays. The vibration directions of these rays are not the same as before, however, because of the altered orientation of the crystal and because vibration directions must be normal to the direction of propaga-

tion (JB). The extraordinary ray must, by definition, vibrate in a plane including the direction of propagation and the optic axis AC. Thus, the vibration direction of the extraordinary ray will be BK. But the magnitude of the refractive index of the extraordinary ray is given by the magnitude of the vector BK, and, as is obvious, the observed index will be less than ϵ. The ordinary ray, on the other hand, will vibrate in a plane perpendicular to that of the extraordinary ray. Its vibration direction and magnitude are represented by BL. However, since the vibration directions of the ordinary ray are all radii of the circular section, $BL = BG$ and the observed refractive index for the ordinary ray remains unchanged, *i.e.*, the crystal will show the index ω. Similar constructions may be made for any orientation of the crystal, or its "hypothetical inner ellipsoid," that show the magnitude of the observable refractive indices. For the measurement of these indices, of course, the stage must be turned so that the vibration plane of the desired ray is north-south.

At this point, the explanation of the definition of the optic axis becomes apparent if a ray traveling along AC is considered. Such a ray would be resolved into components BF and BG, which are both equivalent to ω. Thus the crystal will exhibit only the index ω regardless of rotation about AC.

Note that the ellipsoid is prolate if $\epsilon > \omega$ and oblate if $\omega > \epsilon$ (see Fig. 232).

170. The Concept of Birefringence and Sign.—The birefringence of a uniaxial crystal is simply the numerical difference $\epsilon - \omega$. This difference is positive if ϵ is larger than ω, and negative if ω is the larger. The sign of the birefringence is called the optic sign or "sign of the crystal." It is an easily measured characteristic which is of diagnostic value.

In Sec. 164, the concept of fast and slow rays was mentioned briefly, and, in repetition, it may be said that the fast ray actually travels faster through the crystal, which then has the lower refractive index for the fast ray. Therefore, if the extraordinary ray of a crystal is the fast ray, then ϵ will be smaller than ω and the sign of the difference $\epsilon - \omega$ will be negative. Conversely, if the extraordinary ray is the slow ray, the sign is positive. To determine the optic sign, it is necessary to find out whether the ordinary or the extraordinary ray is the slow ray.

When light from the polarizer enters a uniaxial crystal that is not at extinction, it is resolved into an ordinary and an extraordinary ray, one of which will be the slow ray. As these two rays go through the crystal, the slow ray lags behind the fast ray, *i.e.*, it is retarded. At the point of emergence from the crystal, the slow ray may lag one wave length of, say, red light behind the fast ray (see Fig. 233). The two rays, shown vectorially in Fig. 234 as *OF* and *OS*, vibrating in mutually perpendicular planes, proceed, in phase, up to the analyzer, which resolves them into rays *OF'* and *OS'*, which are equal and opposite vibrations and which cancel each other. Therefore, the vibrations of red light are eliminated from the white light passing through the

FIG. 233.—Section of a crystal (side view).

system, with the result that the crystal appears bluish green. If the phase difference due to retardation were one wave length of *blue* light instead of red, then blue would be eliminated and the crystal would appear orange. A retardation or phase difference of 2, 3, 4, · · · *n* wave lengths will, of course, produce a similar

FIG. 234.—Schematic view along axis of microscope.

interference when *n* is a whole number. If the wave length of blue light is taken as 450 mμ, then blue light will be removed by interference when the retardation is 450, 900, 1,350, · · · *n*(450) mμ, as shown in Table 19. The complementary hues differ slightly according to the value of *n*. If, on the other hand, the

TABLE 19.—RETARDATIONS AND RESULTING POLARIZATION COLORS FOR
DAYLIGHT ILLUMINATION

Retardation, mμ (1 mμ = 10 A)	Color eliminated	Resulting polarization color	Order
0	....	Black	
200	....	Gray	
		White	
350	....	Yellow	First
	Blue		
450	....	Orange	
500	....	Red	
550	Yellow	Violet	
650	....	Blue	
700	Red	Green	
800	Violet	Yellow-green	Second
900	Blue	Yellow	
1,000	....	Orange	
1,100	Yellow	Dark bluish red	
1,200	Violet	Blue-green	
1,300	....	Green	
	Blue		
1,400	Red	Yellow-green	Third
1,500	....	Purplish red	
1,600	Violet	Purple	
1,700	....	Tinted grays of high order	

phase difference is one-half wave length or a fractional multiple of wave lenght, no interference will take place (see Fig. 235).

From the foregoing considerations, it is seen that the interference tint or polarization color produced by a given crystal is a function of the retardation or lag of the slow ray behind the fast ray. This retardation is obviously governed by the thickness and birefringence of the crystal, $\epsilon - \omega$, and not so obviously by the orientation of the crystal. The latter factor is more readily understood by referring back to Sec. 169 and Fig. 231, whence it appears that the apparent value of ϵ becomes smaller as the optic axis of the crystal is turned in the direction shown. The apparent birefringence becomes zero when the optic axis coincides with the direction of propagation of the entering light, *i.e.*, when the optic axis is vertical on the stage of the microscope.

(The term birefringence, of course, refers to the maximum birefringence.)

A useful equation correlates the factors of thickness and orientation of the crystal, mentioned above, and may be used for estimating either apparent birefringence or thickness

$$R = T(\epsilon - \omega)$$

where R = retardation, mμ.

$\quad\quad T$ = thickness, mμ (=10^{-6} mm.).

171. Determination of Sign.—It is obvious that if we increase the thickness of a crystal that shows, say, a first-order yellow interference color, the retardation will thereby increase and the interference color will rise to red, blue, or green, etc., as the thickness of the crystal is progressively increased. In the same way, if we superpose a crystal giving, say, a first-order red tint and a crystal giving first-order gray so that their slow ray vibrations are parallel, then the resulting interference color will be of higher order, viz., blue. Thus reinforcement or "addition" of inter-

Fig. 235.

ference colors indicates similar orientation of the two slow rays (and therefore of the two fast rays also). Similarly, if the slow ray of one crystal is vibrating at right angles to the slow ray of the other, then the retardations will cancel each other or "subtract," with an attendant decrease in the order of the resulting interference color.
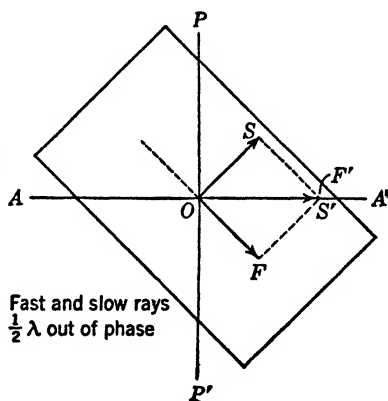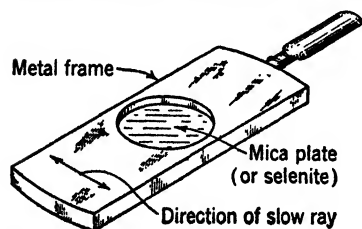
Fig. 236.—A typical form of compensator.

The foregoing discussion leads logically to the conclusion that if we have a crystal plate ("compensator") upon which the direction of vibration of the slow ray is marked (Fig. 236) then, by superposing this plate on an unknown crystal, we can deter-

mine from the change in interference colors the direction of vibration of the slow ray in the unknown crystal. It has already been stated, however, that the extraordinary ray vibrates in the plane of the optic axis and that the optic axis is always the c axis in uniaxial crystals. Therefore, if we find that when the c axis of the unknown crystal is placed parallel to the slow ray of the compensator, reinforcement of the interference colors occurs, then the c axis must be the vibration direction of the slow ray in the crystal. Since the extraordinary ray vibrates in the plane of the c axis, the extraordinary ray of the crystal must be the slow ray, and the crystal is therefore positive.

In tabular form, the reasoning would be as follows:

1. When the slow ray of the compensator is parallel to the c axis of the crystal, the interference color rises. (Observed.)

2. Rise in interference color indicates that slow rays are parallel; hence the c axis must be the vibration direction of the slow ray.

3. But the extraordinary ray vibrates in the plane of the optic axis, or c axis by definition; hence the extraordinary ray must be the slow ray of the crystal.

4. If the extraordinary ray is the slow ray, then ϵ must be larger than ω, since refractive index varies inversely with velocity.

5. If ϵ is larger than ω, then $\epsilon - \omega$ is positive; hence, by definition of sign, the crystal is positive.

Note that this method of determining the sign is useless unless the crystal is sufficiently well defined so that the c axis is recognizable. In case the c axis is not recognizable, the longest direction of the crystal is chosen. If the slow ray vibrates lengthwise of the crystal, the *sign of elongation*, so-called, is positive. With few exceptions, the sign of elongation of uniaxial crystals is the same as the optic sign.

Several types of compensators are available. The mica quarter-wave plate which shows first-order gray is used for observations of crystals showing low birefringence. A selenite (gypsum) plate is more generally applicable. This compensator gives the "sensitive tint" of first-order red. A more elaborate device is the quartz-wedge, or combination-wedge, compensator which gives in succession all tints up to the third order or higher. Other devices for estimating birefringence are described by Johannsen.[8]

Experimental.—1. To illustrate the effect of birefringence on polarization color, examine slides of the following crystals, or

fragments which should be of comparable thickness. Look up the refractive indices in each case: $NaClO_3$, NH_4ClO_4, SiO_2, $CaSO_4$, $NaNO_3$, $CsNO_3$.

2. To illustrate the effect of orientation on polarization color, observe a piece of mica under a very low-power objective or with no objective. Tilt the mica with the fingers. Study a slide of sodium nitrate prepared by fusion. The thin, shapeless (anhedral) crystals are oriented at random, but all are of the same thickness. Try cleaving the mica into thinner plates, and observe the change in color.

3. Place the selenite compensator on the stage, and rotate until the vibration direction of the slow ray (marked on the frame) is northwest by southeast. Note the color of the field. Place the mica compensator in the slot provided, observing that its slow ray is northeast by southwest and that subtraction should therefore result. Note the color of the field, then rotate the stage 90°. Note the change to a higher order color, indicating that the slow ray vibration directions are now parallel.

4. Place a slide of salicin, nitroguanidine, or acenaphthene on the stage. Rotate until some one crystal is in the 45° position (northwest by southeast or northeast by southwest). Using crossed Nicols, observe the polarization color, if any. Place a mica compensator in the slot provided. Observe the color of the field and the color of the crystal. Is the crystal of higher or lower order than before? Is it higher or lower than the color of the field? Rotate the crystal to the other 45° position, *i.e.*, 90° from the original direction. Again note the colors. Repeat, using other crystals on the same slide, then use the selenite plate, and then the quartz wedge. The foregoing procedure should be employed in every case. Use of only one compensator frequently leads to erroneous results.

5. Choose a crystal with tapering edges that show concentric color halos. Align the crystal in a 45° position, introduce the quartz wedge slowly, and note whether the color halos move toward or away from the thin edges. Turn the stage 90°, and repeat. If the colors move toward the thin edges, does this indicate addition or subtraction?

6. Determine the birefringence of a thin crystal of acenaphthene or of a piece of cellophane by the following procedure (after Johannsen[8]): Place the crystal in the 45° position, or 45°

from extinction.   Insert the quartz wedge, and note the color changes.   If subtraction is not observed, rotate the stage 90°. Insert the compensator until compensation occurs, being marked by the appearance of a black bar across the crystal.   Remove the slide from the stage, but do not disturb the compensator. The center of the field should now show the original color of the crystal.   Observe this color closely, then withdraw the wedge slowly, counting the number of times the field becomes red, *i.e.*, determine the order of the color.   Obtain the retardation value from Table 18.   By measuring the thickness of the crystal (see Chap. IV), calculate the birefringence, or, if the birefringence is known, calculate the thickness.

172. Pleochroism.—When a uniaxial crystal is placed on the stage so that the optic axis is horizontal and coincident with the vibration plane of the polarizer, then, as we have seen, the crystal transmits only the extraordinary ray.   Similarly, if the optic axis is horizontal and at right angles to the vibration direction of the polarizer, then only the ordinary ray is transmitted.   If the crystal shows a difference in the velocity at which it transmits light in these positions, it is called anisotropic, but if it also shows a difference in the *degree of absorption* of light (analyzer out), it is called *dichroic*, or, more generally, *pleochroic*.   Thus, a dichroic crystal might be opaque to the ordinary ray and transparent to the extraordinary ray, or vice versa.   More frequently the difference exhibits itself as a variation in hue, one ray appearing, perhaps, yellow and the other red.   (This fact would be denoted by the "pleochroism formula," *e.g.*, ϵ = red, ω = yellow.)

In uniaxial crystals, the optic axis and the normal thereto are the directions of maximum or minimum absorption, or *absorption axes*, and, as one would expect, a section of a pleochroic substance shows no pleochroism when viewed along the optic axis.

In view of the fact that the optical properties of biaxial crystals have not yet been treated in detail, it may only be said at this point that there may be three absorption axes and three possible pleochroic colors (trichroic).   In the orthorhombic system, the crystal axes and absorption axes coincide; in the monoclinic system, only the *b* axis coincides with an absorption axis; and in the triclinic system, there is no necessary relation between the two sets of axes.   (Compare character of extinction, Sec. 167.)

It is probable that the axis of greatest absorption of a crystal containing an organic chromophore group is parallel to the chromophore bond, as in azobenzene, whereas in colored crystals of inorganic materials there is a similar relation to the "direction of distortion."

Experimental.—1. Examine slides of copper acetate, tourmaline, *o*-nitrophenol, butyraldehyde-phenylhydrazone, or iodoquinine sulfate. (The latter material is the active principle of polaroid.)

2. Determine the pleochroic formula of copper acetate or tourmaline, given the optic sign.

UNIAXIAL INTERFERENCE FIGURES

173. Thus far, the treatment of optical crystallography has dealt with well-formed crystals whose optical directions are
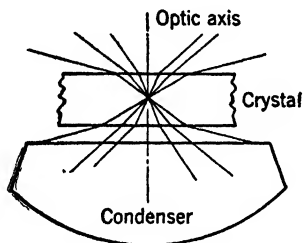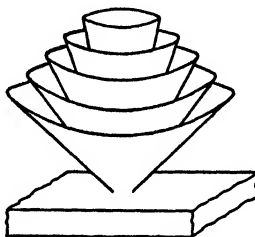
FIG. 237.   FIG. 238.

ascertained by inspection and observation of extinction character. The discussion that follows treats of the methods whereby it is possible to ascertain the optical directions in crystalline fragments that possess none of the geometrical or outward attributes of crystals.

If a thin section of a uniaxial crystal is mounted on the stage of a polarizing microscope with the optic axis vertical, the crystal behaves as though isotropic and remains dark in all positions between crossed Nicols. As we have seen, this is due to the passage of light along the optic axis. If now, however, we illuminate the fragment with strongly converging polarized light from a short-focus condenser, most of the converging rays of light entering the crystal will not pass through parallel to the optic axis (Fig. 237) and separation of the ordinary and extraordinary rays will occur, with resulting production of interference colors.

As shown in the figure, the more convergent the ray, the longer is its passage through the crystal, the greater the retardation, of the slow ray relative to the last ray and hence the higher the order of the interference color.   Figure 238 shows the positions of cones of different retardation, the innermost corresponding to, say, first-order yellow, the second to first-order red, and the third to second-order blue, etc.   In Fig. 239, we are looking down at these cones or at the interference figure itself.   Note
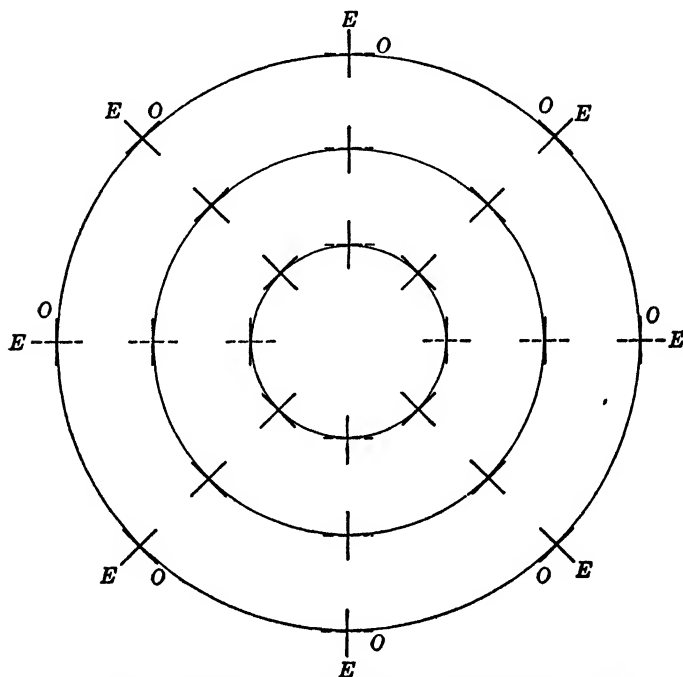
Fig. 239.—Vibrations of extraordinary and ordinary rays.

that in accordance with the rules discussed in Sec. 164 the extraordinary ray E is vibrating in a plane including the direction of propagation and the optic axis of the crystal, whereas the ordinary ray O vibrates in a normal plane.   In other words, the extraordinary ray vibrates radially in the figure and the ordinary ray tangentially.

Since there is no east-west component in the vibration of light from the polarizer, it is obvious that the crystal cannot produce any east-west component by resolution, which fact is illustrated

in Fig. 239 by the dotted lines.   Further, the analyzer permits no north-south vibrations to pass, with the net result that the north-south, east-west directions in the interference figure will be dark, as shown in Fig. 240.   The dark bars, or *isogyres*, correspond then to the vibration planes of the polarizer and analyzer. The *isochromatic curves* correspond to different retardations encountered in the crystal and are of lowest order near the center of the figure.   From these considerations, it is apparent that the appearance of the figure is not changed by rotation of the stage.

The uniaxial figure serves to distinguish isotropic substances from uniaxial crystals whose optic axis is vertical.   It will be recalled that in the latter case the uniaxial crystal appears dark
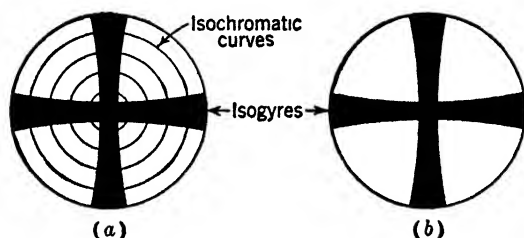
Fig. 240.—Uniaxial optic axis figure.   (a) Thick or highly birefringent crystal. (b) Thin or weakly birefringent crystal.

between crossed Nicols and cannot be distinguished from an isotropic crystal by observations in parallel light (orthoscopic observation).

In order to view the interference figure, it is necessary to look at the aperture rather than the image plane of the objective since all rays coming through the crystal with the same degree of convergence are "focused" in the aperture.   The aperture may be examined by removing the ocular and looking at the rear of the objective (Lasaulx method), by means of a *Bertrand lens* mounted in the body tube and supplementing the ocular, or by means of a hand lens placed above the ocular (Klein or Becke method).   A third method, used when no condenser is available, is to place a minute glass sphere (0.1 mm. diameter) directly over the crystal or cover glass.   In this latter case, the interference figure is observed just above the glass sphere, without the use of auxiliary lenses.[8]

A modification of the Becke method is used when it is necessary to isolate the interference figure of one small crystal in a crowded field. A blackened diaphragm of sufficiently small aperture is placed in the ocular at the focal plane of the eye lens, and the crystal is moved on the stage until its image falls within this aperture. The Becke lens, which is a 10× positive ocular
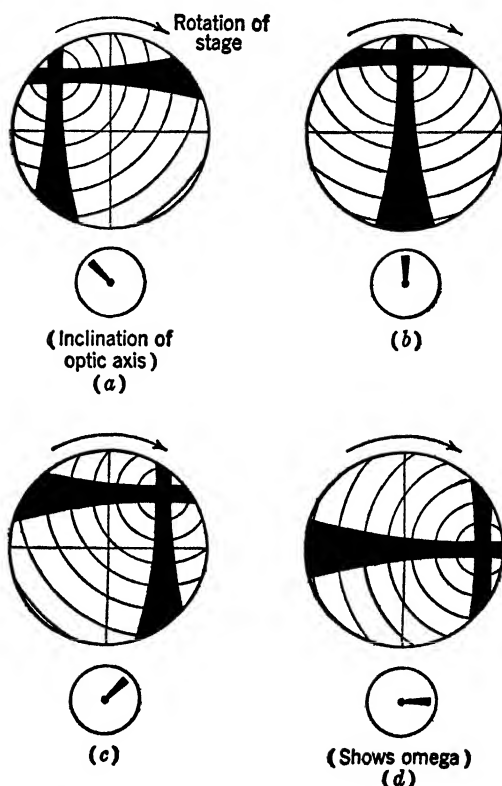
Fig. 241.—The inclined uniaxial optic-axis figure.

or hand magnifier, is placed over the eyepiece, and the interference figure of the single crystal is viewed alone.

174. The Inclined Optic-axis Figure.—When the optic axis of the crystal under examination is not exactly vertical, but is inclined slightly to one side, the resulting interference figure is displaced toward that side, and the center of the dark cross and colored curves is simply moved away from the center of the field of view (Fig. 241). In slightly inclined figures, the center

of the cross is still within the field of view, but if the crystal is tilted farther away from the normal position, the center may be moved outside the limits of the field, and only an arm of the cross will be seen. If the stage is rotated, the optic axis is rotated about the axis of the microscope, but the position of the isogyres relative to the optic axis is fixed; hence the arms of the cross will remain north-south and east-west and will successively sweep across the field of view as the stage is rotated (see Fig. 241).

175. Determination of Optic Sign.—The orthoscopic method of determining the sign was discussed in Sec. 170. Note that
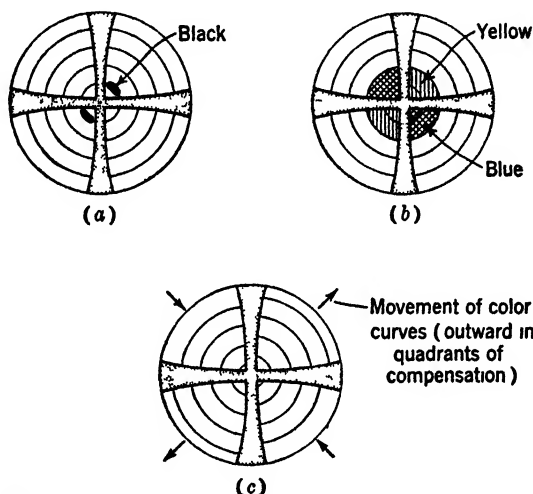
FIG. 242 —Effect of compensators on the optic-axis figure of a negative crystal·
(*a*) mica ½λ plate, (*b*) selenite first-order red plate; (*c*) quartz wedge.

as stated, this method is useful only in the case of well-developed crystals where the optic directions are readily identified. When only irregular fragments are available, conoscopic methods must be used (converging illumination). In Fig. 239, the vibration directions of the ordinary and extraordinary rays are represented by short lines radial and tangential with respect to the figure. Since, in determining sign, it is only necessary to find which is the slow ray, the procedure resolves itself to the following: If a compensator with its slow ray vibrating northeast-southwest is placed over the figure, compensation will occur in two opposite quadrants and addition will occur in the other pair of quadrants. If addition occurs in the northeast-

southwest quadrants, where the extraordinary-ray vibration is parallel to the slow-ray direction of the compensator, then the extraordinary ray must be the slow ray, and the substance is positive. Obviously, in the other quadrants (northwest-southeast), the slow rays are not parallel, and compensation results. A convenient rule to remember is the following: if a line joining the quadrants of compensation makes a plus sign with the slow ray of the compensator, then the crystal is positive. This rule is also applicable to inclined figures, provided that the point of emergence of the optic axis (center of cross) is in a 45° position, as in Fig. 241a and c.

The quadrants of compensation may be recognized by a lowering of the color order. In the case of the mica compensator, this change is marked by a pair of black dots near the center of the cross (Fig. 242a); with a selenite compensator the color is yellow (Fig. 242b); and with the quartz wedge the colors move outward in the quadrants of compensation (Fig. 242c).

176. Refractive-index Measurements.—When light travels parallel to the optic axis of a uniaxial crystal, the crystal behaves like an isotropic substance and shows only the refractive index ω. Thus a fragment that shows a centered optic-axis figure shows only ω when viewed orthoscopically (*i.e.*, in parallel light). If the figure is not centered, ω may be observed only when the optic axis tilts east-west, *i.e.*, when the center of the cross is east or west (Fig. 241d) (see Sec. 169). Since the retardation is at a maximum when the optic axis is horizontal and at a minimum when the optic axis is vertical, the approximate inclination of the optic axis may be inferred from the interference tint of the crystal itself. When the optic axis is vertical, the crystal is dark; when it is slightly inclined to the vertical, the color is gray-white, etc.; and when the optic axis is horizontal, the crystal displays its highest interference colors (dependent also on thickness).

It is possible to compute the value of ϵ by observing the refractive index n_i of a crystal whose optic axis is slightly inclined north-south at an angle ϕ to the vertical. Such a crystal will show an inclined optic-axis figure such as Fig. 241b. The angle ϕ is computed by measuring, with an ocular micrometer, the distance D from the center of the field to the center of the dark cross. The relation

$$\sin \phi = \frac{kD}{\omega}$$

is then applied, the value of constant k having been determined for the microscope by using a crystal of known refractive indices. The value of ϕ is used in the equation of Salomon[19,8] (see also Fox and Finch[17]).

$$n_\iota = \frac{\epsilon\omega}{\sqrt{\epsilon^2 \sin^2 \phi + \omega^2 \cos^2 \phi}}$$

177. The Flash Figure.—When the optic axis is horizontal on the stage, an interference figure known as a flash figure results (Fig. 243). This consists of two poorly defined dark hyperbolas that flash in and out of the field very rapidly as the stage is rotated. The optic axis turns into the quadrants where the isogyres leave the field on clockwise rotation. The isogyres come together and meet in the center of the field, to form a diffuse cross at the extinction position, when the optic axis is north-south or east-west. From the preceding rules, the location of the optic axis and the determination of the sign are comparatively simple matters. The procedure in the latter case is to locate the optic axis, place it northwest-southeast, or 45° from the extinction position, remove the Bertrand lens and upper condensing lens, and then observe the color changes in the fragment when a compensator is inserted. The sign is, of course, determined by noting whether the optic axis is the vibration direction of the fast or slow ray, as discussed in Sec. 171. The refractive index ϵ may be measured on fragments showing a flash figure by placing the optic axis north-south at extinction and ω may be measured if the optic axis is placed east-west.

TABLE 20.—SUMMARY OF UNIAXIAL INTERFERENCE FIGURES

Optic-axis figure, centered..........	Optic axis vertical. Crystal shows ω in all positions of stage. Sign from figure
Optic-axis figure, inclined..........	Optic axis tilted away from vertical toward center of cross. Crystal shows ω when an isogyre is east-west. Sign from figure or from specimen
Flash figure.....................	Optic axis horizontal, turns into quadrants where isogyres leave. Crystal shows ϵ when optic axis is north-south, ω when optic axis is east-west. Sign obtained from specimen only
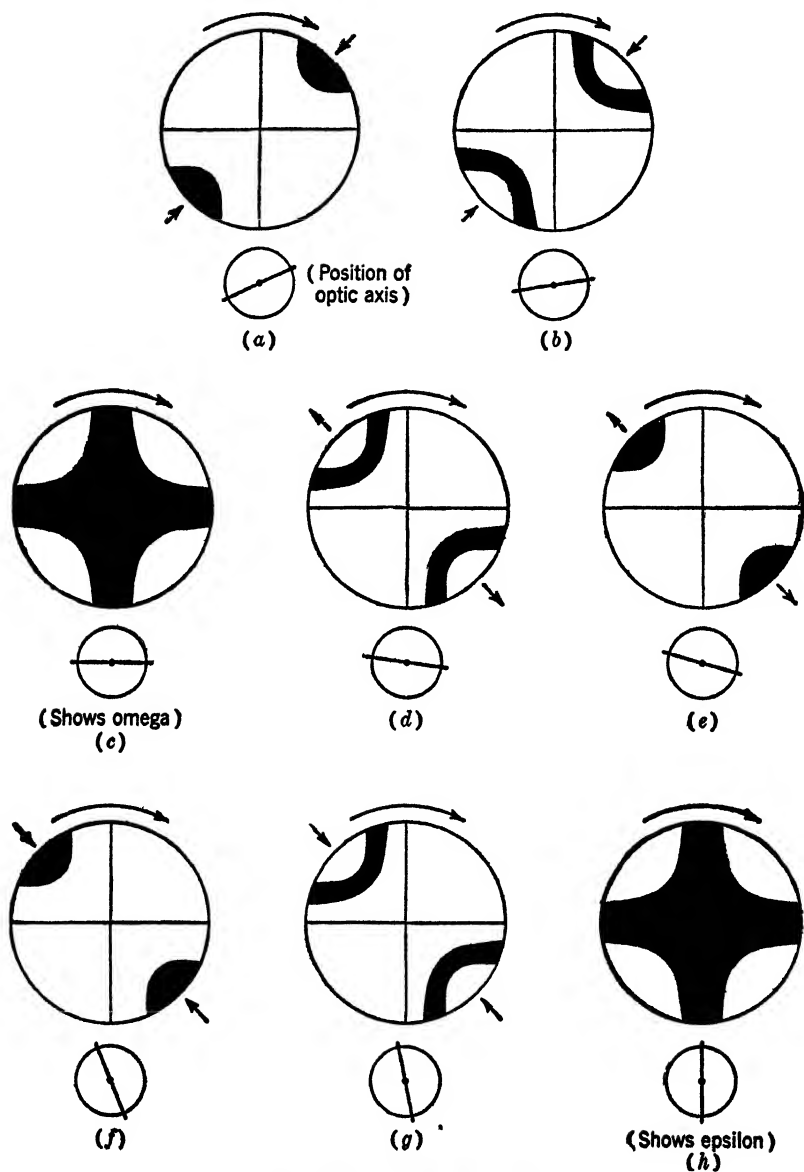
FIG. 243.—The flash figure.

Experimental.—Observe interference figures on slides obtained from the instructor.[1]   Correlate orientation of crystal, character of extinction, interference tint, and birefringence with the appearance of the figure.   Obtain the sign of each crystal examined, and be able to tell how the crystal should be oriented for measurement of refractive indices.   For crystals showing flash figures, the sign is determined from the specimen itself by means of compensators.   It is best to choose a crystal of such size that it does not occupy the entire field of view, so that the color of the field may be compared with the color of the crystal when a compensator is inserted.   Choose, if possible, a crystal with tapering edges, so that movement of the color fringes may be observed when the quartz wedge is inserted.   This method is the best for determination of compensation (see Sec. 171).

178. Identification of Uniaxial Substances.—The theoretical discussion of the preceding pages may now be summarized and put to use in the analytical determination of uniaxial crystals. The process of analysis will vary, of course, with the nature of the specimen, but the following outline may serve as a general guide.

Experimental.—1. Observe the original material under a low-power objective; note color, homogeneity, particle size, evidence of crystallinity, etc.   Estimate solubility in water and kerosene. Warm a portion in a micro test tube to ascertain the presence of water of crystallization.

2. Crystallize from a suitable solvent; well-formed crystals about 0.05 to 0.5 mm. in size should be obtained.   Since this step is, by and large, the hardest to carry out and the most ·wasteful of material, it is advisable to use crushed and sieved fragments rather than crystals if only a small sample is available. The fragments should, however, be tested for solubility in immersion media.   If sufficient sample is left after the optical properties of the fragments have been studied, then the residue may be crystallized and the crystals studied in the light of the data already obtained on the fragments.

3. Mount the crystals, or particles, in a suitable medium, and look for interference figures.   Roll the particles, if necessary, by pushing the cover glass sideways.   Check the sign on at least

[1] See list at end of chapter.

three different figures. Estimate the indices by the relief shown by suitably oriented crystals then measure to ± 0.002 by the Becke method. It is best to check the orientation by the type of interference figures shown, but it is possible to measure the two indices shown at the extinction positions by all grains with high polarization colors. The highest and lowest indices so measured should be noted. The index of the dark fragments (optic axis vertical) is then measured and is ω. If ω corresponds to the highest value, then the substance is negative and ϵ is the lowest index measured. If ω is the lowest value, the sign is positive and ϵ is the highest index. This method is used only when interference figures are hard to obtain. For precise work, obtain centered flash figures for measurement of ϵ. Note that ω may be measured for any fragment at one extinction position (see index ellipsoid, Sec. 169).
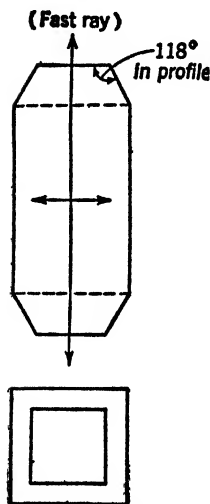
(Fast ray)
118°
In profile

Fig. 244.

4. If the substance can be obtained in well-formed crystals of the proper size, examine these for system, habit, and relation of optic directions to crystallographic axes. Sketch a few typical crystals, measuring silhouette angles and showing the position of the fast and slow rays by long and short arrows superposed on the sketches (Fig. 244).

5. Note any special characteristics such as pleochroism, variations in habit, or markings.

BIAXIAL CRYSTALS

179. When a ray of light enters a biaxial crystal, it is resolved into two polarized rays, vibrating in mutually perpendicular planes. Both of these rays, however, are extraordinary rays, *i.e.*, they do not obey the usual laws of refraction. There are three mutually perpendicular planes in a biaxial crystal, in which three extraordinary rays may vibrate, and these planes determine the so-called axes of elasticity of the crystal. In Fig. 245, these axes are designated by their usual symbols X, Y, and Z, whereas the Greek letters α, β, and γ represent the refractive index shown by the crystal for rays vibrating in the X, Y, and

Z directions.   Note that $\alpha < \beta < \gamma$.   (These refractive indices are sometimes denoted by $N_p < N_m < N_g$.)

If a ray of light enters the crystal along XO, it is resolved into two rays: one, characterized by the refractive index β, vibrates along OY; the other, γ, vibrates along OZ.   Similarly, light passing into the crystal along ZO is resolved into rays showing indices α and β, and light entering along YO is resolved into rays showing indices α and γ.   Note that, if the ray enters the crystal in any direction included in the plane XOY, it is resolved into a ray vibrating along OZ showing a constant index γ and a ray vibrating in the plane XOY showing an index that varies

between α and β, the variation depending on the direction of the entering ray.   The situation is analogous for rays entering in planes YOZ and XOY.   Thus in each of these planes, one ray shows a constant index, the other shows a varying index.

FIG. 245.—Vibration planes—biaxial.

180.   As was the case for uniaxial crystals, the rules relating to refractive indices are most conveniently summarized in the index ellipsoid or biaxial indicatrix (Fig. 246), which is an ellipsoid with three unequal axes.   In the diagram, the three axes of the ellipsoid correspond to the axes of elasticity referred to above, and the rule may be stated as follows: when light enters a biaxial crystal along, say, AO, the semi-axes OY and OL of the section L normal to the direction of the entering ray give the refractive indices and the vibration directions of the two rays formed.

Consideration of the geometry of the ellipsoid will reveal that for one orientation of AO, L will be a circle, of radius $OL = \beta$.   If this is the case, then the crystal will exhibit only the single refractive index, OL or β, provided that light enters along AO.   From the symmetry of the ellipsoid, it is obvious that there are two such directions AO and $A'O$ both in the plane XZX' and equally inclined to OZ.   By analogy to the concept for uniaxial crystals, these directions are called optic axes and the acute angle

between them is called *the optic angle*. The axis bisecting the acute angle between the optic axes is called the *acute bisectrix* and is a vibration direction. The axis bisecting the obtuse angle between the optic axes is the *obtuse bisectrix*, and the axis normal to the plane of the optic axes (optic plane) XZX'
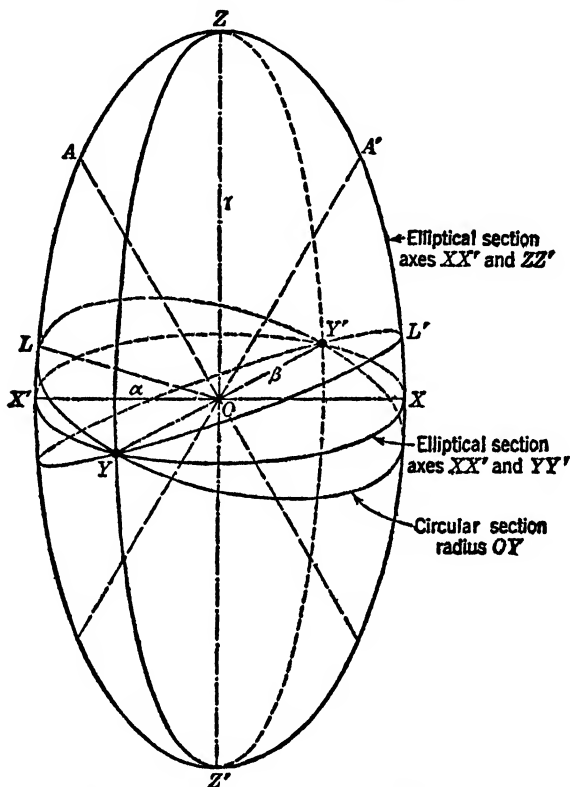
Fig. 246.—Index ellipsoid for a biaxial crystal (+).

is the *optic normal*, OY or β. The two bisectrices and the optic normal are the three vibration directions; *the optic axes are not*.

181. Optic Sign.—A biaxial crystal is said to be positive if γ vibrates along the acute bisectrix, or since γ is always the largest refractive index, if the acute bisectrix is the vibration direction of the slow ray. Note that XZX' (Fig. 246) is always the optic plane and that, therefore, the acute bisectrix may be either X, which is the vibration direction of the smallest index α, or Z, which is the vibration direction of the largest index γ. Thus

the optical indicatrix of a positive crystal is a prolate ellipsoid (Fig. 246), but for a negative crystal it is an oblate ellipsoid (Fig. 247).

The sign of a biaxial crystal may be determined in just the same way as that of a uniaxial crystal, except that the acute bisectrix is used as a reference instead of the optic axis.   For a uniaxial crystal, the sign is positive if the optic axis is the vibration direction of the slow ray.   For a biaxial crystal, the sign is positive if the acute bisectrix is the vibration direction of the slow ray.   To carry out the analogy, the uniaxial optic sign is
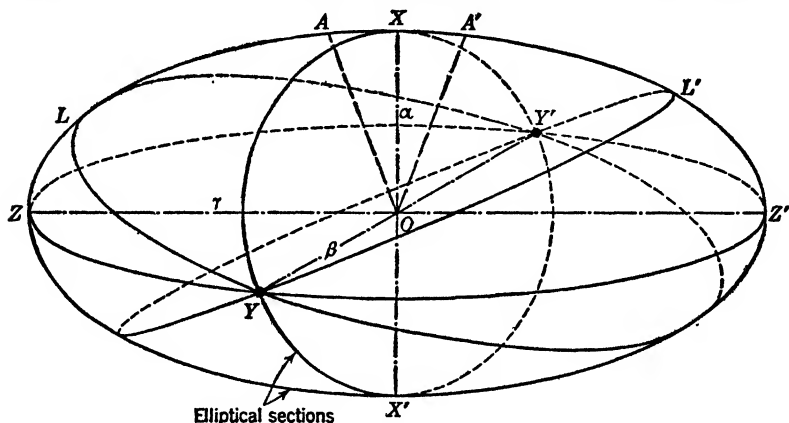
FIG. 247.—Index ellipsoid for biaxial crystal (−).

the sign of the birefringence $\epsilon - \omega$.   For biaxials, the sign is obtained from the sign of the expression

$$(\gamma - \beta) - (\beta - \alpha) = \text{birefringence}$$

(Location of the acute bisectrix is accomplished by means of interference figures which will be discussed later on.)

182. Measurement of Refractive Indices.—The rule formerly applied to uniaxials holds true also for biaxials; *viz.*, if an optical direction (axis of elasticity) may be placed horizontal and north-south on the stage of a polarizing microscope, the crystal then shows the index of refraction characteristic of that optical direction.   Thus, with reference to Fig. 247, if a negative crystal is oriented with its acute bisectrix horizontal and north-south, it will give the refractive index α.   A positive crystal similarly oriented gives γ.   Both positive and negative crystals show β

when the optic normal is horizontal and north-south or when light travels along an optic axis.

BIAXIAL-INTERFERENCE FIGURES

183. Biaxial-interference figures are named for the optical direction that is vertical on the stage and serve the same purposes as the uniaxial figures. It is most convenient to regard the crystal as an index ellipsoid, with the proper direction vertical,

(a)
Melatope or "eye"

(b)

(c)
Extinction position
(Obtuse bisectrix N.-S)

(d)

(e)
Extinction position
(Optic normal N.-S.)
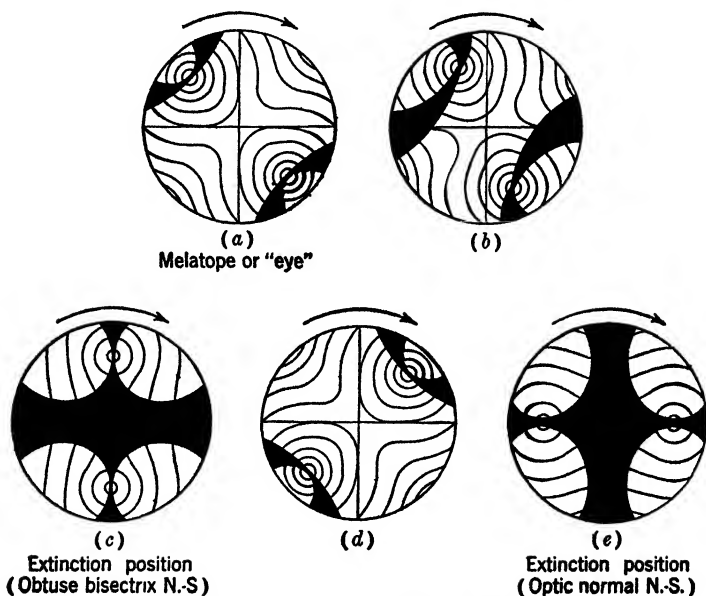
FIG. 248.—The acute-bisectrix figure.

and if this is done, the relation of the refractive indices, etc., may be readily visualized once the orientation of the ellipsoid is established.

184. The Acute-bisectrix Figure.—This figure (Fig. 248) is reminiscent of the uniaxial optic-axis figure in that it usually displays isochromatic curves, concentric, not about a single optic axis, but about two optic axes. The isogyres of the figure are hyperbolic and move in and out as the stage is rotated, meeting in the center when the optic plane is north-south or east-west (extinction position), and separating until their vertices pass through the points of emergence of the optic axes, at the 45°

position (see Fig. 248*a* and *d*).   If the optic angle is small, the
vertices will remain within the field at their maximum separa-
tion, but if the optic angle is fairly large, the vertices will be
outside of the field at the 45° position (see Fig. 251).   It is
possible to recognize this figure even if the color curves are
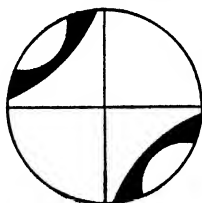
FIG. 249.—Acute
bisectrix figure, for
thin or weakly bire-
fringent specimen.

FIG. 250.—Small
optic angle.
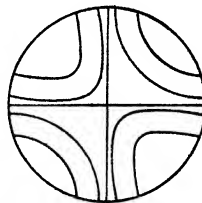
FIG. 251.—Large
optic angle.

absent, by the rate of disappearance of the hyperbolas.   By using
a 4-mm. 0.65 N.A. objective, the isogyres leave the field from
the extinction position in 22 to 45° rotation of the stage.   For a
higher N.A. objective, the limits are considerably larger.

Determination of Sign.—The figure is turned to a 45° position,
and a compensator inserted.   Compensation of the isochromatic
curves occurs in two opposite
quadrants, addition occurs in the
other quadrants (Fig. 252).   The
theory of compensation is similar
to that for the uniaxial optic-axis
figure, and the same rule applies,
*viz.: if a line joining the quadrants
of compensation makes a plus sign
with the slow ray of the compensator,
the crystal is positive.*   It is also
possible to determine the sign on
the specimen itself.   Place the
optic plane in the northwest-
southeast position (Fig. 248*a*)

FIG. 252.—Movement of colors with
quartz wedge (positive crystal).

either by observation of the "eyes" of the figure or by
using the rule that the optic plane enters the quadrants
where the isogyres move out on clockwise rotation.   (Compare
with the uniaxial flash figure.)   When the optic plane is in the
northwest-southeast position, then the obtuse bisectrix is

horizontal and northwest-southeast. Remove the condenser and Bertrand lens, and determine whether the obtuse bisectrix is the slow or the fast ray, by means already discussed (Sec. 171).

Measurement of Refractive Indices.—If the acute bisectrix is vertical, then the obtuse bisectrix and optical normal are horizontal. The usual rule applies that whenever an optic direction is horizontal and north-south on the stage, its characteristic refractive index is shown. Thus if the obtuse bisectrix is north-south, either α or γ may be measured, the choice depending on the sign of the crystal. If the optic normal is north-south, β may be measured, irrespective of the sign of the crystal.

Measurement of Optic Angle.—The distance between the eyes of the figure or the distance between the vertices of the hyperbolas at their maximum separation is dependent on the optic angle. As shown in Fig. 253, however, the optic angle in air ($2E$) is always larger than the true optic angle
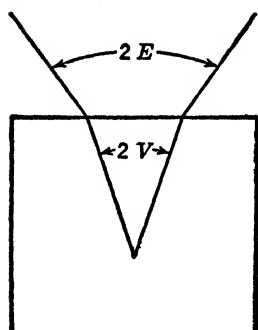
Fig. 253.—Relation of $2E$ to $2V$.
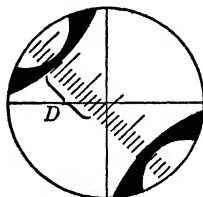
Fig. 254.

($2V$) owing to refraction at the surface of the crystal, the relation being given by Snell's law as $\sin E / \sin V = \beta$. The optic angle in air may be measured by determining the maximum distance $2D$ between the melatopes, using an ocular micrometer scale (Fig. 254). Then according to Mallard's equation,

$$D = K \sin E$$

where K is a constant characteristic of the microscope, which may be determined experimentally. Objectives of large numerical aperture may be used for measuring optic angles up to about 160° ($2E$). Perhaps the best method of measuring a large optic angle is that of Johannsen.[8] A substance of known $2E$ is placed on the top of the condenser and is adjusted so that its optic plane is in the 45° position. The specimen is placed on the stage and oriented similarly so that the two

interference figures are superposed. The stage is now rotated until the vertices of the isogyres of the "unknown" figure coincide with the visible isogyres of the reference figure. The reading of the stage scale is then noted, the reference crystal is removed from the condenser, and the stage is rotated until the extinction position of the isogyres is reached. The reading of the scale is taken, and the difference of the two readings then equals d in the formula

$$\sin E \text{ unknown} = \frac{\sin E \text{ reference}}{\sqrt{\sin 2d}}$$

Dispersion of the Optic Axis.—Owing to variation of refractive index with wave length, the optic angle depends on the color
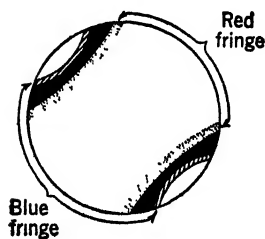
FIG. 255.- $r > v$ Dispersion.
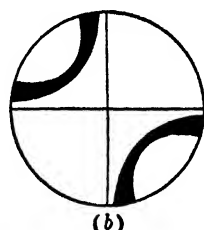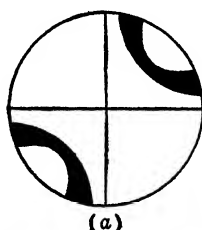
FIG. 256.—Crossed-plane axial dispersion. (a) In blue light. (b) In red light

of the illuminating light. When the optic angle is greater for red light, then the convex or inner side of the hyperbolas will be tinted red when white light is used, and the concave side of the hyperbolas will be bluish. This phenomenon is commonly referred to as $r > v$ dispersion (Fig. 255) and often aids in characterizing a crystal. $v > r$ dispersion is also found.

This type of dispersion is related to that shown by isotropic materials, but for a biaxial crystal, there are three variable indices that determine dispersion

$$\cos^2 V = \frac{\gamma^2(\beta^2 - \alpha^2)}{\beta^2(\gamma^2 - \alpha^2)} \quad \text{or} \quad \cos^2 V = \frac{\alpha^2(\gamma^2 - \beta^2)}{\beta^2(\gamma^2 - \alpha^2)}$$

where V = optic angle.

In cases where dispersion of this type occurs to a marked degree, and when β is numerically close to either α or γ, it is possible for the indices to vary sufficiently with wave length so that for some color β equals α or γ and the crystal becomes

uniaxial. Further change in wave length causes reappearance of biaxial character, but the optic plane will now be normal to its original position (Fig. 256). This phenomenon is known as crossed-plane dispersion and is not uncommon among organic crystals.
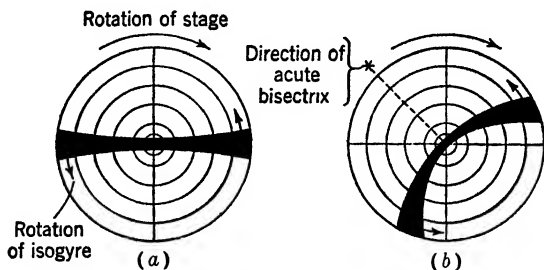
Fig. 257.—The biaxial optic-axis figure.

More complicated types of dispersion may occur in monoclinic and triclinic crystals, for which see Johannsen.[8]

185. The Biaxial Optic-axis Figure.— If light passes through a biaxial crystal along either of the optic axes, an interference figure similar to those shown in Figs. 257 and 258 is produced. This figure is entirely analogous to the uniaxial optic-axis figure, save that it has only a single isogyre which rotates about the optic
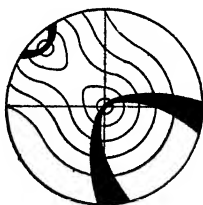
Fig. 258.—Relation to acute bisectrix figure shown by crystal with small optic angle.
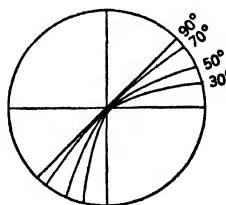
Fig. 259.—Method for estimating $2V$ from curvature of the isogyre.

axis as the stage is turned. The curvature of the isogyre at the 45° position depends on the optic angle and serves as a rough measure of $2V$ (see Fig. 259). For more accurate methods, see Johannsen.[8] When the isogyre is north-south or east-west, it is straight and indicates the trace of the optic plane. (Note that the optic plane and the isogyre rotate in different directions.)

At intermediate positions, the acute bisectrix lies on the convex side of the isogyre.

Determination of Sign.—Orient the acute bisectrix in the northwest position by placing the convex side of the isogyre pointing in that direction. When a compensator is inserted, compensation is marked by movement of the colors away from the acute bisectrix. If compensation occurs along the northwest-southeast direction, the crystal is positive (Fig. 260).

Measurement of Refractive Index. Crystals showing this figure give β in all positions.

186. The Obtuse-bisectrix Figure.—This figure is entirely analogous to the uniaxial flash figure except that the isogyres do not move as rapidly (Fig. 261). In general, the isogyres leave the field from the extinction position in 12 to 18° rotation of the stage, for a 4-mm. 0.65 N.A. objective.

Fig. 260.—Movement of colors with quartz wedge (positive crystal). Compare Figs. 242 and 252.

Determination of Sign.—The sign is usually determined on the specimen and not on the figure. The rule is that the acute
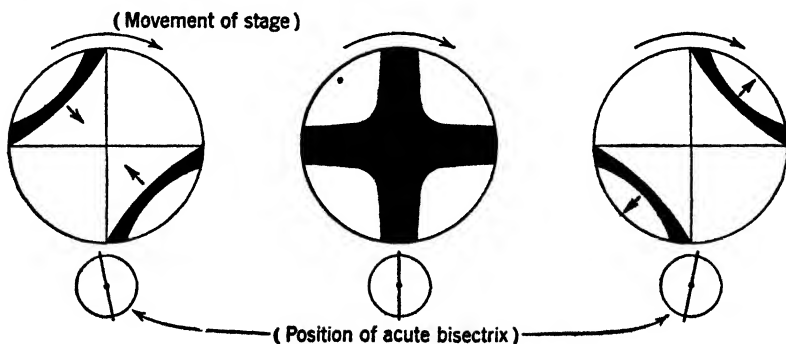
Fig. 261.—The obtuse-bisectrix figure.

bisectrix turns into the quadrants that the isogyres leave on the clockwise rotation. Once the acute bisectrix is located approximately, the condenser and Bertrand lens are removed, and the stage is rotated to the nearest extinction position, when the acute bisectrix will be north-south or east-west, as the case may

be.   The stage is then turned to the 45° position, and by means of compensators it is possible to determine whether the acute bisectrix is the slow or the fast ray (Sec. 171).

Measurement of Refractive Indices.—Since the acute bisectrix and optic normal are horizontal, it is possible to determine α or γ, and β on fragments showing an obtuse-bisectrix figure.

187. The Optic-normal Figure.—This figure is also analogous to the uniaxial flash figure, and its isogyres move just as rapidly. In general, the diffuse isogyres leave the field, from extinction, in 5 to 10° rotation of the stage, for a 4-mm. 0.65 N.A. objective.
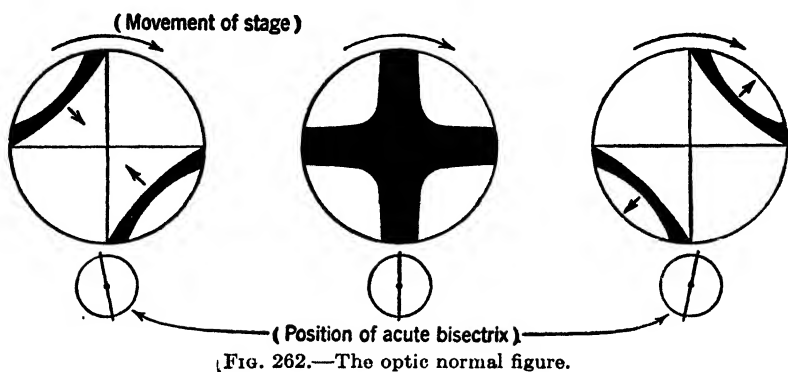
Fig. 262.—The optic normal figure.

Determination of Sign.—The acute bisectrix enters the quadrants where the isogyres leave on clockwise rotation.   The acute bisectrix is located as above, and the sign is determined on the specimen.

Measurement of Refractive Indices.—The optic plane is horizontal on the stage, thus permitting the acute and obtuse bisectrices to be placed north-south.   Both α and γ may be measured on crystals showing an optic normal figure.

188. Experimental.—1. The Acute-bisectrix Figure: Use a thick section of mica, and examine the interference figure. Observe the relation of the extinction positions to the positions of the hyperbolas and the positions of maximum separation of the hyperbolas.   Point out the trace of the optic plane and the optic normal.   Given the numerical aperture of the 4-mm. objective as 0.65, the angular aperture is calculated to be about 80° (see Sec. 101).   Hence, if the vertices of the hyperbolas are at the edge of the field at the 45° position, $2E$ is approximately

80°. If $\beta = 1.6$, what is $2V$? Determine the sign both on the figure and on the specimen. Repeat with thinner sections and with various other crystals. Watch for dispersion of the optic axes in the case of p-nitrobenzaldehyde and sodium tungstate. Using the Mallard or Johannsen method, measure $2E$ for several specimens.

2. The Optic-axis Figure: Examine several crystals. Estimate the optic angle, determine the sign. What factors determine the number of concentric isochromatic curves visible?

3. The Obtuse-bisectrix Figure: Note the rotation of the stage required to move the isogyres out of the field from the extinction position. Determine the sign on several specimens. (Note that the sign may be obtained from the figure itself but the rule is just the opposite of that for the acute-bisectrix figure.)

4. The Optic-normal Figure: Measure the rotation of the stage necessary to move the isogyres away from the position of the cross. Determine the sign on several specimens.

189. Inclined and Uncentered Biaxial Figures.—If a crystal is oriented so that two optic directions are horizontal, the crystal shows a centered interference figure and two refractive indices may be measured, as we have seen from Secs. 184 to 187. If, however, the crystal tilts in such a way that only one optic direction is horizontal, then an inclined figure results and only one
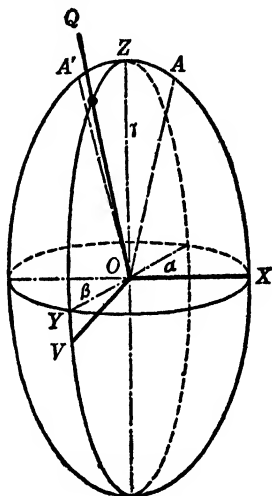
. FIG. 263.—Theory of the inclined figure. In this case a positive crystal viewed along QO (as in Fig. 264) will show the index α when OX is placed north-south, since the normal OX to the path QO equals α. Note that OV does not equal OY, hence the index β will not be shown.

refractive index is observable. Thus, in Fig. 263, if light travels along QO, which is vertical, the obtuse bisectrix OX is horizontal, and may be placed north-south for measurement of α. No other index may be measured since no other optic direction is horizontal. Other possibilities are shown in Figs. 265 and 266. In all these cases, it is necessary that an optic direction be horizontal in order that a refractive index may be measured, and this condition is easily ascertained by examining the figure.

If an optic direction is horizontal, then at extinction the inter-
ference figure will show a single straight isogyre passing through
the center of the field and at right angles to the vibration direc-
tion in question.   These facts are illustrated by Figs. 264 and 265.

190. Optic Orientation.—The optic orientation of a crystal is
the relationship existing between the optic directions and
crystallographic axes.   This relation is usually expressed in the
form of a sketch such as Figs. 267 and 268, in which arrows and

(a)   (b)
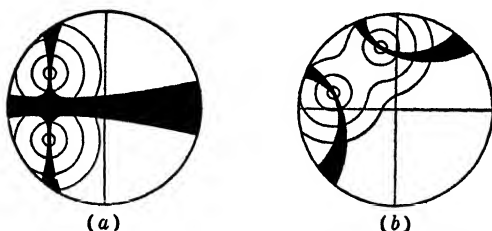
Fig. 264.—The inclined figure.   (a) The obtuse bisectrix is horizontal and
north-south; therefore its characteristic index may be measured.   (b) Effect
of 45° rotation of the stage.   Note the curvature of the isogyres.

(a)   (b)   (c)
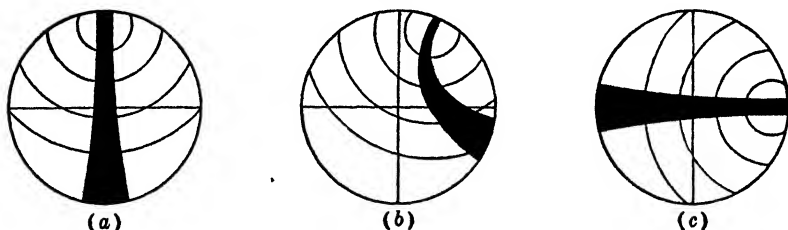
Fig. 265.—The inclined optic-axis figure.   (a) Optic normal horizontal and
east-west.   (b) Stage rotate 20° clockwise.   (c) Optic normal horizontal and
north-south.   Measure β.

dotted lines are used to indicate optical directions.   It might be
noted that certain abbreviations and symbols are used that
have not yet been discussed, *e.g.*:

B X A = acute bisectrix.
B X O = obtuse bisectrix.
O.A. = optic axis.
O.N. = optic normal.
Opt. Pl. = optic plane.
$\wedge$ = "makes an angle with."
X, Y, Z = "axes of elasticity," or vibration directions of α, β, γ,
respectively (Sec. 179).   The two sets of terms are used
interchangeably.

Note again that in the orthorhombic system the optical and crystallographic directions all coincide; in the monoclinic system,
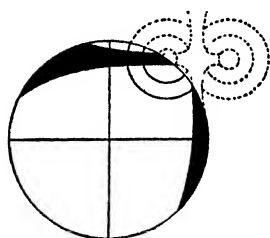
FIG. 266.—The uncentered figure at extinction position. (No index measureable.)
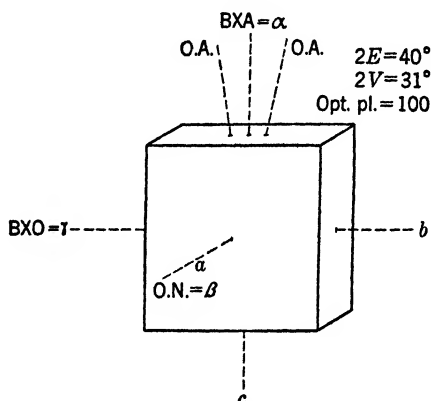
FIG. 267.—Optic orientation.

the b axis alone coincides with an optic direction; whereas in the triclinic system there is no necessary relationship. The correlation of extinction character with interference figures permits
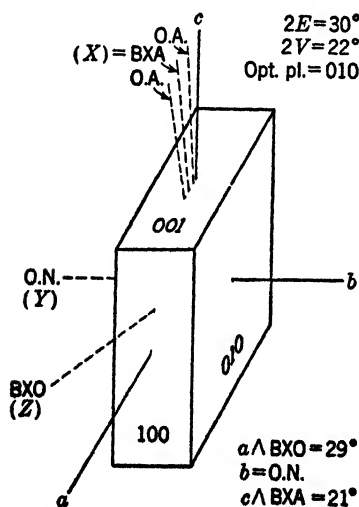
FIG. 268.—Optic orientation.
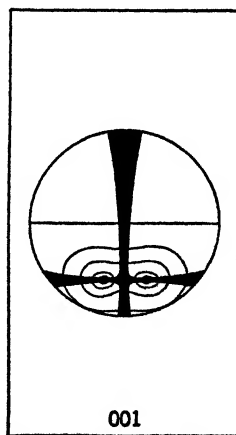
FIG. 269.

definite classification of crystals according to system (see Prob. 3*b*).

Some authors prefer to sketch the profiles of the crystals and on each profile superpose a sketch of the interference figure shown, *e.g.*, Fig. 269.

191. The universal stage, mentioned previously, is particularly useful for refined studies of the optical properties of crystalline materials. This elaborate and expensive device permits orientation of the specimen in any desired position, thereby making it possible to measure all refractive indices, optic angle, extinction angles, etc., with a single crystal. A concise summary of the uses of this device is given by Winchell,[6] and further details are to be found in a series of papers by Emmons,[5] who designed the improved model.
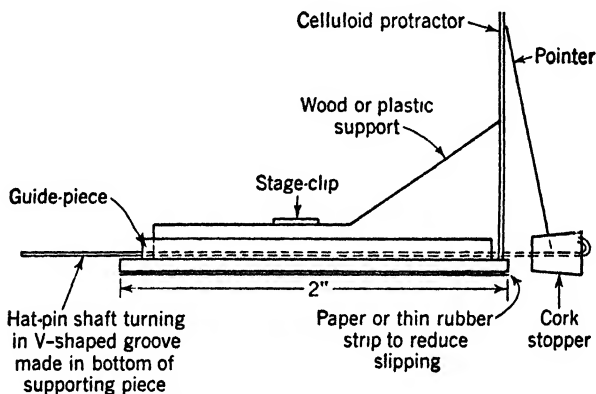
Fig. 270.—Simplified rotation device (side view).

Simplified Rotation Apparatus.—The advantages of a device whereby a crystal may be rotated about a horizontal axis during observation are obvious, especially when the crystal is acicular. Although the universal stage is most satisfactory for the purpose, there are several less expensive makeshifts. The excellent apparatus of Wood and Ayliffe[20] is inexpensive and quite satisfactory. A still simpler design is shown in Figs. 270 to 272. This rotation device employs a fine needlelike axis to which the crystal is attached by means of a bit of dental wax, "household cement," or other adhesive. The crystal is then immersed in the index liquid and rotated until a suitable interference figure is obtained. Since an acicular crystal presents all its indices on rotation about the long axis, it is possible to measure these with one setting of a single crystal. In addition, the optic

angle $2V$ may be measured on most crystals by noting the rotation necessary to bring first one and then the other optic axis to the center of the field.

The simplest of all rotation devices consists of a thin-walled fine glass capillary. The crystal is placed in the capillary together with a drop of index liquid, and the whole is immersed
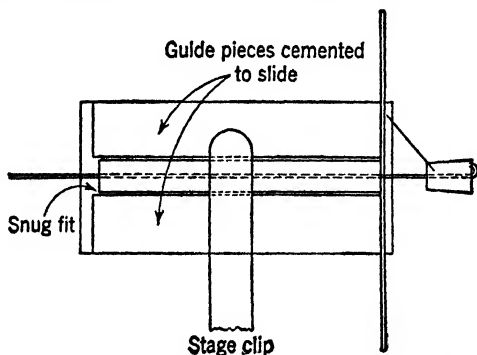
FIG. 271.—Simplified rotation device (top view).
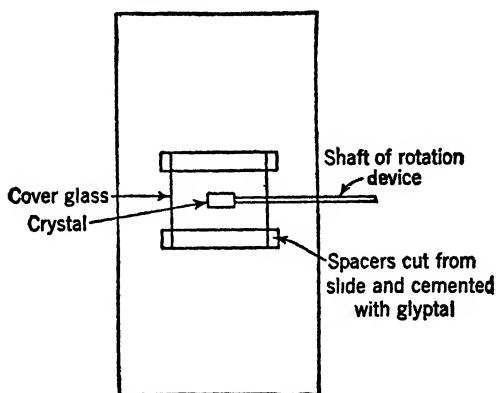
FIG. 272.—Cell.

in a cell similar to that used with the rotation apparatus shown in Fig. 272. Motion is secured by rolling the capillary.

192. Identification and Characterization.—The general procedure outlined in Sec. 178 is again employed but with some modifications made necessary by the increased complexity of the problem.

After carrying out steps 1 and 2 of the procedure, the crystals or particles are mounted, as before, in a suitable medium and

interference figures are located.   Make several checks on the sign from as many different figures as convenient.   Measure the optic angle if possible.   It is usually a valuable aid to the determination.   Estimate the three indices, and, by trial and error, determine these indices by the immersion method, using interference figures to ascertain orientations.   The following table may be useful.

TABLE 21.—RELATION OF BIAXIAL FIGURES TO MEASURABLE REFRACTIVE INDICES

Interference figure	Sign	Indices measurable at extinction
Centered B X A.......	$+$ $-$	α and β γ and β
Centered O.A..........	$\pm$	β only, irrespective of position of isogyre
Centered B X O.......	$+$ $-$	γ and β α and β
Centered O.N........	$\pm$	α and γ
Inclined B X A........	$+$ $-$	α or β when isogyre is straight and coinciding with east-west cross hair γ or β when isogyre is straight and coinciding with east-west cross hair
Inclined O.A..........	$\pm$	β when isogyre is straight and coinciding with east-west cross hair
Inclined B X O.......	$+$ $-$	γ or β when isogyre is straight α or β when isogyre is straight

Note that it is not necessary to know which index is being measured since α is always the smallest, β intermediate, and γ the largest.   In view of this fact, it is obvious that a statistical study of a large number of random-oriented particles at extinction positions would give α as the lowest index measured and γ as the highest, whereas β would be the mode or most frequent value observed on grains showing lowest polarization color. This method may be used without recourse to interference figures but is very tedious.

If the sample under observation consists of needlelike crystals, it is advisable to mount a crystal on a simple rotation device.

Obtain the extinction character, extinction angles, silhouette angles, and optic orientation of all well-formed crystals.   Sketch a number of crystals, illustrating habit, optic orientation, pleochroism, etc.

Simplified Routine for Characterization of Crystals.—A simple set of directions for characterizing crystals is often desired by chemists who wish to characterize crystalline material for purposes of description or partial identification.   Although the nontechnical procedure which follows is not as rigorous as the unabridged method, it provides sufficient data for many purposes. Inclusion of such data in published work is greatly to be desired since a partial crystallographic description is of great assistance in subsequent identification of complicated or unstable materials. In inorganic chemistry such data may constitute as definite an identification as the melting point constitutes in organic chemistry.   The organic chemist will' often find partial determination of optical properties as good a criterion of identity as the preparation of a "derivative."   The abridged method is particularly useful in qualitative analytical work when the sample is known to be one of several possible substances which are available for comparison or whose properties have been tabulated.

1. Prepare well-defined crystals preferably between 0.05 mm. and 1 mm. in cross section.   These may be prepared in a drop on the microscope slide (p. 241), in which case several specimen slides should be made, or the crystals may be formed in a small test tube.   In any case, the conditions of crystallization should be noted.   The crystals are mounted in an inert medium of comparable refractive index, if possible (Tables 14, 15, and 16).

2. Examine with a microscope of moderate power.   Sketch representative types and measure profile angles which are repeated or characteristic (Sec. 135).   Note the habit (Fig. 203).

3. With polarizer in place but without analyzer, examine crystals in different positions.   If a color change is apparent the crystals are pleochroic (Sec. 172).

4. Examine between crossed nicols.   If crystals are dark in all positions proceed to step 8.   If thin crystals show bright colors, the birefringence is great.   If relatively thick crystals show untinted whites, grays, or yellows, the birefringence is small.   Record.

5. Determine the character of extinction between crossed nicols (Sec. 167).   If the extinction is oblique, measure the extinction angle for several specimens.

6. If crystals are elongated and colored between crossed nicols, determine the sign of elongation for several specimens.

Place a crystal in a northwest-southeast position between crossed nicols and introduce a compensator. If the color of the crystal changes to a lower order (Sec. 171 and Table 19), the sign of elongation is positive and vice versa. If possible, check with several compensators and repeat with the crystal northeast by southwest, when opposite effects should be noted. If crystals show no well-marked color changes, they are either too thick or too thin.

Extinction	Interference figure	Crystal system
I. Isometric................	None	Isometric (cubic)
II. Some isometric, others not:		
a. Others show parallel ext.	Uniaxial flash (Fig. 243)	Tetragonal or hexagonal or rhombohedral
b. Others show symmetrical ext. only	Uniaxial O.A. inclined (Fig. 241)	Rhombohedral
c. Crystals showing isometric ext. 4 or 8-sided	Uniaxial O.A. cent. (Fig. 240)	Tetragonal
d. Crystals showing isometric ext. 3 or 6-sided	Uniaxial O.A. cent. (Fig. 240)	Hexagonal or rhombohedral
III. Parallel and symmetrical only:		
a. Parallel...............	Biaxial cent. (Figs. 248, 249, 257, 261, 262)	Orthorhombic
b. Symmetrical..........	Biaxial inclined (Figs. 264, 265)	Orthorhombic
IV. Parallel, symmetrical, oblique:		
a. Parallel...............	Biaxial inclined (Figs. 264, 265)	Monoclinic
b. Symmetrical..........	Biaxial uncent. (Fig. 266)	Monoclinic
c. Oblique..............	Biaxial cent. (Figs. 248, 249, 261, 262)	Monoclinic
d. Isometric (rare).......	Biaxial O.A. cent. (Figs. 257, 258)	Monoclinic
V. All oblique..............	Biaxial uncent. (Fig. 266)	Triclinic

Explanation of Table.—Each roman numeral designates the character of extinction shown by a group of random-oriented crystals. The meaning of the description in the middle column is given below:

Uniaxial flash: Vague shadows which meet in the center of the field and retreat very rapidly in opposite quadrants as the stage is rotated.

Uniaxial O.A. inclined: Dark cross or single arm of cross, always parallel to north-south east-west cross hairs and always straight.   May be tapered.

Uniaxial O.A. centered: Dark cross whose center is center of field.   Does not move.

Biaxial centered: See illustrations in text.   Usually well-defined hyperbolas which meet in center of field and retreat as stage is rotated.

Biaxial inclined: Dark bar or bars which sweep across field.   Parallel to and coincident with cross hair at two positions, otherwise usually curved. Also biaxial centered type when hyperbolas do not meet in center of field.

Biaxial uncentered: Curved bar or bars not described above which never coincide with cross hair.   Also biaxial hyperbolic type whose dark bars are never coincident with a cross hair, and which do not meet in center of field.

Biaxial O.A. cent: Single bar, often curved, which revolves about center of field as an axis.

7. Using a 4-mm. 0.65 N.A. objective, observe the interference figure shown by isolated crystals.   This is viewed with the aid of a Bertrand lens, or by removing the ocular and looking down at the back of the objective.   A short-focus condenser is used, and the nicols must be crossed.   Identify by name by comparison with figures given in the text.   If the figure is well defined, sketch over previous sketch of crystal.   Note in the preceding table that the crystal system may now be identified.

8. If crystals are isotropic, the refractive index is measured as in Sec. 157.   If centered interference figures are obtained, refractive indices may be measured at the two extinction positions as directed in Sec. 168.   These are reported simply as "larger," "intermediate," and "smaller" index.

9. If interference figures show well-marked color curves (Figs. 242, 252, 260), the optic sign is determined by means of a compensator, preferably a quartz wedge.

10. If an acute bisectrix or biaxial optic axis figure (Figs. 248, 250, 257) is obtained, the optic angle in air $2E$ may be estimated (Sec. 184) or the true optic angle $2V$ (Fig. 259).

193. Experimental.—1. Distinguish mixtures of

$$\begin{cases} NaClO_3 \\ KCl \end{cases} \quad \begin{cases} KClO_3 \\ NaCl \end{cases} \quad \begin{cases} Na_2WO_4 \\ KClO_3 \end{cases} \quad \begin{cases} urea \\ KNO_3 \end{cases} \quad \begin{cases} nitroguanidine \\ salicin \end{cases}$$
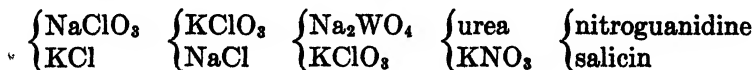
Look up properties in each case.

2. Given a group of six well-crystallized samples of various materials and a sample of "unknown" which is one of the group, identify the unknown without measuring refractive indices.

3. Identify a powdered biaxial crystalline material by examination of the irregular particles (see references listed below and tables at end of chapter).

4. Given a fairly pure sample of "unknown," recrystallize and characterize the crystals as completely as possible. It is important to report the conditions of crystallization in detail.

Sources of Optical Crystallographic Data

"International Critical Tables," Vol. I, Vol. VII.

A. N. Winchell, "Microscopic Characters of Artificial Solid Substances or Artificial Minerals," Part II, John Wiley & Sons, Inc., New York, 1931.

E. S. Larsen, *U.S. Geol. Survey Bull.* 848 (1934).

W. H. Fry, Tables for the Microscopic Identification of Inorganic Salts, *U.S. Dept. Agric. Bull.* 1108 (1922).

P. Groth, "Chemische Kristallographie," Vols. I–IV, W. Engelmann, Leipzig, 1906–1919.

Landolt-Bornstein, "Physikalisch-chemische Tabellen," W. A. Roth and K. Scheel, eds., Verlag J. Springer, Berlin, 1923–1934.

SUPPLEMENTARY TABLES OF REFRACTIVE INDEX AND NOTES ON EQUIPMENT

TABLE 22.—REFRACTIVE INDEX TABLES—INORGANIC

Isotropics

Formula	n	Formula	n
KF.....................	1.352	NaCl..................	1.544
LiF.....................	1.392	KBr...................	1.559
KCN..................	1.410	$Sr(NO_3)_2$..............	1.567
CaF_2..................	1.434	$Ba(NO_3)_2$..............	1.571
Na alum...............	1.439	CsBr..................	1.582
$Na_3PO_4 \cdot 10H_2O$..	1.450	$NaBrO_3$...............	1.617
NaCN..................	1.452	NH_4Cl................	1.639
K alum................	1.456	NaBr..................	1.641
NH_4 alum..............	1.459	CsCl..................	1.642
KCl....................	1.490	KI....................	1.667
RbCl..................	1.494	NH_4I.................	1.703
$NaClO_3$................	1.515	NaI...................	1.774

Uniaxial Positive

Formula	ω	ϵ	Formula	ω	ϵ
$Na_3PO_4 \cdot 12H_2O$.......	1.446	1.452	$Na_3VO_4 \cdot 10H_2O$.......	1.540	1.547
$K_2S_2O_6$..............	1.455	1.515	SiO_2................	1.5442	1.5533
$Na_3AsO_4 \cdot 12H_2O$......	1.459	1.467	$CsNO_3$..............	1.55	1.56
$Na_3VO_4 \cdot 12H_2O$.......	1.509	1.523	Li_2SiO_3.............	1.591	1.611
$LiAlSi_2O_6$.............	1.514	1.521	$SrSiO_3$..............	1.599	1.637

Uniaxial Negative

Formula	ω	ϵ	Formula	ω	ϵ
$BeSO_4 \cdot 4H_2O$.........	1.472	1.439	$AlCl_3 \cdot 6H_2O$..........	1.560	1.503
$LiKSO_4$................	1.4723	1.4717	Na_2SO_3	1.565	1.515
$CoSO_4 \cdot 6H_2O$.........	1.495	1.460	KH_2AsO_4............	1.567	1.518
KH_2PO_4..............	1.509	1.468	$Be_3Al_2Si_6O_{18}$.........	1.580	1.574
$NiSO_4 \cdot 6H_2O$.........	1.511	1.487	$NaNO_3$.............	1.587	1.336
$NH_4H_2PO_4$..........	1.525	1.479	$Na_2Mg(CO_3)_2$........	1.594	1.54
$K_2Ca(CO_3)_2$..........	1.530	1.480	$K_2Mg(CO_3)_2$.........	1.597	1.47
$Ba(ClO_4)_2 \cdot 3H_2O$......	1.533	1.532	$Ca_5F(PO_4)_3$..........	1.632	1.629
$SrCl_2 \cdot 6H_2O$..........	1.536	1.487	$CaCO_3$..............	1.658	1.486
$NaLiCO_3$.............	1.538	1.406			

TABLE 22.—REFRACTIVE INDEX TABLES—INORGANIC.—(*Continued*)
Biaxial Positive

Formula	System	α	β	γ	Optic angle, deg.
$NaH_2PO_4 \cdot 7H_2O$	M	1.441	1.442	1.453	$2E = 57$
$NH_4NaHPO_4 \cdot 4H_2O$	M	1.439	1.442	1.469	$2V = 35.5$
$Na_2HAsO_4 \cdot 7H_2O$	M	1.462	1.466	1.478	$2E = 89$
$K_2S_2O_8$	Tr	1.461	1.467	1.566	$2V = 30$
$KHCO_3$	M	1.38	1.482	1.57	$2V = 81.5$
NH_4ClO_4	O	1.482	1.483	1.488	$2E = 112$
K_2SO_4	O	1.493	1.495	1.497	$2E = 111$
$(NH_4)_2S_2O_8$	M	1.498	1.502	1.587	$2V = 24$
$Na_2S_2O_3 \cdot 5H_2O$	M	1.489	1.508	1.536	$2E = 154$
$CaSO_4 \cdot 2H_2O$	M	1.520	1.523	1.530	$2V = 58$
$(NH_4)_2SO_4$	O	1.521	1.523	1.533	$2E = 84$
$Na_2WO_4 \cdot 2H_2O$	O	1.553	1.553	1.570	$2V = 25$
$CaSO_4$	O	1.571	1.575	1.613	$2V = 44$
$SrSO_4$	O	1.622	1.624	1.631	$2V = 51$
$BaCl_2 \cdot 2H_2O$	M	1.635	1.646	1.660	$2V = 85$

Biaxial Negative

Formula	System	α	β	γ	Optic angle, deg.
$Na_2SO_4 \cdot 10H_2O$	M	1.394	1.396	1.398	$2E = 122$
$Na_2HPO_4 \cdot 12H_2O$	M	1.432	1.436	1.437	$2E = 87$
$Na_2HAsO_4 \cdot 12H_2O$	M	1.445	1.450	1.451	$2V = 65$
H_3BO_3	Tr	1.340	1.456	1.459	$2V = 7$
$NaH_2PO_4 \cdot 2H_2O$	O	1.440	1.463	1.481	$2V = 83$
$Na_2B_4O_7 \cdot 10H_2O$	M	1.447	1.469	1.471	$2E = 56$
$Li_2SO_4 \cdot H_2O$	M	1.459	1.477	1.488	$2V = 78$
$NaH_2PO_4 \cdot H_2O$	O	1.456	1.485	1.487	$2E = 44$
$ZnSO_4 \cdot 7H_2O$	O	1.457	1.480	1.484	$2E = 70$
$K_2C_2O_4 \cdot H_2O$	M	1.440	1.505	1.550	$2V = 82$
KNO_3	O	1.335	1.506	1.506	$2E = 11$
$KClO_3$	M	1.408	1.517	1.523	$2E = 43$
$KHC_2O_4 \cdot H_2O$	M	1.415	1.545	1.565	$2V = 37$
$(NH_4)_2C_2O_4 \cdot H_2O$	O	1.438	1.545	1.595	$2V = 64$
$NaH_2AsO_4 \cdot H_2O$	O	1.538	1.553	1.561	$2E = 120$
$CsSO_4$	O	1.560	1.564	1.566	$2E = 116$
Li_2CO_3	M	1.428	1.567	1.572	$2V = 15$
NH_4NO_3	O	1.413	1.611	1.637	$2V = 35$
$KSbOC_4H_4O_6 \cdot 5H_2O$	O	1.620	1.636	1.638	$2V = 42.5$

TABLE 23.—REFRACTIVE INDEX TABLES—ORGANIC
Isotropics

Formula	n	Formula	n
C_3H_7NO................	1.416	$(C_6H_{10}O_5)_x$..............	1.53
$NaC_4H_7O_4$..............	1.457	$[(CH_3)_3N]_2H_2PtCl_6$........	1.600
$C_6H_{11}NO_3$............ . .	1.525	$C_{21}H_{25}NO_4$....	1.635

Uniaxial Positive

Formula	ω	ϵ	Formula	ω	ϵ
CH_4N_2O........	1.484	1.602	$C_6H_{15}PS$..............	1.590	1.650
$C_{10}H_{14}O$........... ..	1.525	1.609	$C_{12}H_{11}NO_2S$..........	1.600	1.649
$C_{16}H_{26}O$..............	1.545	1.548	$C_{14}H_{10}O_2$	1.659	1.678
$C_7H_8O_2$	1.569	1.666			

Uniaxial Negative

Formula	ω	ϵ	Formula	ω	ϵ
$C_{10}H_{20}O$..............	1.497	1.476	$C_{34}H_{50}O_2$....... ,.....	1.579	1.540
$C_3H_{12}N_6O_3$............	1.499	1.490	$C_{11}H_{11}N_2OBr$..........	1.581	1.493
$C_7H_{14}O_6(\beta)$...........	1.529	1.513	$C_6H_6O_2(p)$..	1.633	1.626
C_2H_5NO..............	1.54	1.46	C_6H_6NBr.............	1.646	1.642
$C_4H_{10}O_4$..............	1.544	1.521	$C_4H_4NO_2I$.............	1.696	1.673
$C_{12}H_{20}O$..............	1.545	1.544	$C_{14}H_{12}O$.............	1.717	1.563
$C_4H_8O_2Cl_2$.............	1.554	1.515	CHI_3.................	1.800	1.750
$C_5H_{12}O_4$..............	1.559	1.548			

TABLE 23.—Refractive Index Tables—Organic.—(*Continued*)

Biaxial Positive

Formula	System	α	β	γ	Optic angle, deg.
$C_{12}H_8$...............	O	1.402	1.463	1.617	$2V = 70$
$C_{12}H_{10}$...............	O	1.407	1.468	1.620	$2V = 70$
$C_2H_2O_4$...............	O	1.440	1.475	1.625	$2V = 56$
$C_6H_8O_7 \cdot H_2O$...............	O	1.493	1.498	1.509	$2V = 65$
$C_7H_{14}O_6(\alpha)$...............	O	1.528	1.529	1.537	$2V = 47$
$C_6H_{13}NO_2$...............	?	1.525	1.535	1.560	$2V = 61$
$C_4H_6O_6$...............	M	1.495	1.535	1.604	$2V = 78$
C_6H_8NCl...............	?	1.56	1.57	1.60	$2V = 60$
$C_9H_{11}NO$...............	O	1.560	1.576	1.647	$2V = 51$
$C_4H_8N_2O_8$...............	O	1.549	1.583	1.625	$2V = 86$
$C_9H_{11}NO$...............	O	1.556	1.587	1.700	$2V = 58$
$C_9H_9NO_3$...............	O	1.535	1.592	1.760	$2V = 65$
$C_9H_{11}NO_3$...............	?	1.550	1.600	1.680	$2V = 80$
$C_9H_{11}NO_2$...............	?	1.600	1.610	1.675	$2V = 45$
$C_7H_6N_2$...............	O	1.609	1.612	1.616	$2V = 86$
$C_6H_6O_2(o)$...............	M	1.604	1.614	1.734	$2V = 35$
$C_9H_{11}NO$...............	M	1.495	1.625	1.807	$2V = 88$

Biaxial Negative

Formula	System	α	β	γ	Optic angle, deg.
$C_4H_2O_3$...............	O	1.442	1.478	1.638	$2V = 55$
$C_2H_6O_6$...............	M	1.445	1.505	1.540	$2V = 68$
$C_6H_{12}O_5(H_2O)$...............	M	1.523	1.531	1.534	$2V = 58$
$C_4H_6O_4$...............	M	1.450	1.534	1.610	$2V = 82$
$C_{12}H_{22}O_{11} \cdot H_2O$...............	M	1.517	1.542	1.555	$2V = 70$
$C_2H_8N_2O_4 \cdot H_2O$...............	O	1.439	1.546	1.594	$2V = 61$
$C_{12}H_{22}O_{11}$...............	M	1.537	1.565	1.570	$2V = 48$
$C_{10}H_{13}NO_2$...............	M	1.54	1.571	1.59	$2V = 62$
$C_5H_9NO_4$...............	O	1.490	1.605	1.620	$2V = 40$
$C_{10}H_8O_6S_2$...............	M	1.460	1.614	1.697	$2V = 79$
$C_2H_5NO_2$...............	M	1.495	1.615	1.650	?
$C_8H_6O_4$...............	?	1.436	1.616	1.706	$2V = 63$
$C_6H_6O_2(m)$...............	O	1.578	1.620	1.627	$2V = 46$
$C_7H_6N_2O_4$...............	M	1.442	1.662	1.756	$2V = 59$
$C_7H_5O_2Cl$...............	?	1.446	1.776	1.726	$2V = 45$
$C_7H_5NO_4(o)$...............	?	1.616	1.706	1.756	$2V = 60$
$C_7H_5NO_4(p)$...............	?	1.656	1.726	1.706	$2V = 60$

FORMULA INDEX FOR TABLE 23

CHI_3	Iodoform
CH_4N_2O	Urea
$C_2H_2O_4$	Oxalic acid
C_2H_5NO	Acetamide
$C_2H_5NO_2$	Glycin
$C_2H_6O_6$	Oxalic acid dihydrate
$C_2H_8N_2O_4 \cdot H_2O$	Ammonium oxalate monohydrate
C_3H_7NO	Acetoxime
$C_3H_{12}N_6O_3$	Guanidine carbonate
$C_4H_2O_3$	Maleic anhydride
$C_4H_4NO_2I$	Iodosuccinimide
$C_4H_6O_4$	Succinic acid
$C_4H_6O_6$	Tartaric acid
C_4H_7ONa	Diacetate
$C_4H_8O_2Cl_2$	Erythritol dichlorohydrin
$C_4H_8N_2O_3$	l-Asparagine
$C_4H_{10}O_4$	Erythritol
$C_5H_9NO_4$	d-Glutaminic acid
$C_5H_{11}NO_3$	Bios
$C_5H_{12}O_4$	Pentaerythritol
$C_6H_6O_2(o)$	Catechol
$C_6H_6O_2(m)$	Resorcinol
$C_6H_6O_2(p)$	Hydroquinone
C_6H_6NBr	p-Bromoaniline
$C_6H_8O_7 \cdot H_2O$	Citric acid monohydrate
C_6H_8NCl	Aniline hydrochloride
$(C_6H_{10}O_5)_x$	Starch
$C_6H_{12}O_5(H_2O)$	β-Rhamnose
$C_6H_{13}NO_2$	l-Leucine
$C_6H_{15}PS$	Triethylphosphine sulfide
$C_7H_5O_2Cl$	(p)Chlorobenzoic acid
$C_7H_5NO_4(o)$	(o)Nitrobenzoic acid
$C_7H_5NO_4(p)$	(p)Nitrobenzoic acid
$C_7H_6N_2O_4$	2,6-Dinitrotoluene
$C_7H_6N_2$	Benzimidazole
$C_7H_8O_2$	Guaiacol
$C_7H_{14}O_6(\beta)$	β-Methylglucoside
$C_7H_{14}O_6(\alpha)$	α-Methylmannoside
$C_8H_6O_4$	Terephthalic acid
$C_9H_9NO_3$	Hippuric acid

$C_9H_{11}NO$	*p*-Acetotoluide
$C_9H_{11}NO$	N-Methylacetamide
$C_9H_{11}NO$	*o*-Acetotoluide
$C_9H_{11}NO_2$	*l*-Phenylalanine
$C_9H_{11}NO_3$	*l*-Tyrosine
$C_{10}H_8O_6S_2$	Naphthalene-1,6-disulfonic acid
$C_{10}H_{13}NO_2$	Phenacetin
$C_{10}H_{14}O$	Thymol
$C_{10}H_{20}O$	*l*-α-Menthol
$C_{11}H_{11}N_2OBr$	4-Bromoantipyrine
$C_{12}H_8$	Acenapthylene
$C_{12}H_{10}$	Acenapthene
$C_{12}H_{11}NO_2S$	Benzenesulfanilide
$C_{12}H_{20}O$	Camphor (Matico)
$C_{12}H_{22}O_{11}$	Sucrose
$C_{12}H_{22}O_{11} \cdot H_2O$	Lactose
$C_{14}H_{10}O_2$	Benzil
$C_{14}H_{12}O$	Phenyl *p*-tolyl ketone
$C_{16}H_{26}O$	Guaiol
$C_{21}H_{25}NO_4$	Corydine
$C_{34}H_{50}O_2$	Cholesteryl benzoate

SUPPLEMENTARY NOTES ON EQUIPMENT

194. *For the educational laboratory* (four students):

4 petrographic microscopes with sliding analyzers and Bertrand lenses. [If necessary, any microscope possessing a rotating stage may be adapted to the purpose through the use of Polaroid film[21] for the polarizer and (cap) analyzer. A good condenser of at least N.A. 1 is required.]

4 sets of accessories for the above, including:

Lamp.

Cross-hair ocular.

16-mm. and 4-mm. objectives (latter N.A. 0.65).

Mica, selenite, and quartz-wedge compensators.

1 micrometer ocular, parfocal with above.

2 rotation devices and several cells.

1 set of immersion media.

1 Bravais or Bertrand ocular.

1 oil-immersion objective and matched condenser.

1 set of colored glass filters (and 4 light yellow doublet filters, Wratten Nos. 22 and 58).

1 small agate mortar.

4 sieves about ½ in. diameter, 100 mesh (bolting cloth).

4 individual sets of slides, cover glasses, and forceps (conveniently kept in covered Petri dish).

1 equipment for crystallizing on a slide, comprising:

2 copper blocks, 1 in. square or larger.

Microburner with flame less than 1 cm. high.

Micro watch glass and holder, for sublimations.

2 sets of slides, mounted in balsam unless otherwise noted:

2 sodium chlorate small fragments.

2 potassium chlorate small fragments.

1 potassium chlorate well-formed small crystals.

2 sodium bromate fragments.

2 nitroguanidine crystals.

1 copper acetate crystals.

1 azobenzene crystals.

1 acenaphthene crystals (from benzene, mounted in Karo).

1 copper sulfate pentahydrate crystals.

1 lead iodide crystals.

1 sodium nitrate crystals.

1 ammonium dihydrogen phosphate crystals.

1 potassium alum crystals.

1 oxalic acid dihydrate crystals.

1 salicin crystals.

1 o-acetotoluide.

1 p-acetotoluide.

1 fused sodium nitrate (fuse on slide, and press down cover glass firmly).

1 mica (need not be mounted).

1 cellophane.

1 o-nitrophenol.

1 set of slides kept by instructor and issued to students, labeled A, B, C, etc. (Slides marked * may be purchased from Harold Tomlinson, Swarthmore, Pa.)

Uniaxial Optic-axis Interference Figure:

*Quartz ⊥ Opt. axis.

*Quartz ∥ Rhomb.

*Calcite ⊥ Opt. axis.

*Tourmaline ⊥ Opt. axis.

Sodium nitrate by fusion.

Ammonium acid phosphate crystals.

Sodium nitrate crystals in balsam.

Uniaxial Flash Figures:

*Quartz ∥ prism.

*Calcite ∥ prism.

    *Corundum ‖ prism.
    *Zircon ‖ prism.
    *Tourmaline ‖ prism.
     Nitroguanidine.
  Biaxial Acute-bisectrix Figures:
     *Phlogopite.
     *Muscovite.
     *Topaz.
     *Barite.
     *Epidote.
     *Aragonite.
      Sodium tungstate.
      Acenaphthene.
  Biaxial Optic-axis Figures:
     *Topaz.
      Sugar.
      Benzoic acid.
      Potassium persulfate.
  Biaxial Obtuse-bisectrix Figures:
     *Topaz.
     *Barite.
     *Epidote.
     *Staurolite.
      Cellophane.
  Biaxial Optic-normal Figures:
     *Selenite (gypsum).
     *Tremolite.

Slides of biaxial crystals labeled according to face upon which crystal rests are available* and serve as exercises in determining optic orientation.

1 set of well-defined samples of crystals for use as unknowns. These are conveniently made by cooling and stirring a saturated solution of the substance, or by other conventional procedures such as sublimation.

1 set of crystalline powders for use as unknowns.

1 set of easily crystallized substances for use as unknowns. (To be crystallized on slides by the student.)

The following equipment is desirable for demonstrations:

Models of crystals showing optic and crystallographic directions. (May be made from Lucite or clear Bakelite.)

Three-dimensional index ellipsoids cut from celluloid and marked with acetone-dye ink.

Movable diagrams of interference figures cut from cardboard and suitably colored.

For industrial use:

1 research petrographic microscope or equivalent[21] with accessories as follows:

> 1 lamp.
> 1 Bertrand lens (focusable).
> 1 set of compensators.
> $8\times$ and $15\times$ oculars.
> 16-mm. N.A. 0.25 objective.
> 8-mm. N.A. 0.5 objective.
> 4-mm. N.A. 0.65 objective.
> 2-mm. N.A. 1.25 objective.
> N.A. 1.4 interchangeable condenser.
> 1 coordinate micrometer ocular, parfocal with above.
> 1 Bravais or Bertrand ocular.
> 1 Wright diaphragm for isolating interference figures from small crystals.
> 1 set of filters (Table 2).
> 1 stage goniometer.
> Suitable equipment for preparation of samples.
> 1 set of immersion media.
> 1 mechanical stage.

PROBLEMS

1. If a crystal, shaped roughly like a biconcave lens, is immersed in a liquid of lower index, how will the Becke line move? What will be the effect of the concavity on the half-shadow test?

2. By means of a sketch, show the optics involved in the half-shadow test. Explain why the shadow of the analyzer frame gives the same effect as the shadow of a card held below the condenser.

3. *a.* Why is Canada balsam used in preference to other adhesives to cement the halves of a Nicol prism?

    b. What assumptions are made in classifying crystals by their extinction character?

    c. Is the sign of elongation always the same as the optic sign? Discuss.

4. How many rays pass through a crystal:

    a. When it is extinguished?

    b. When it is not at extinction?

    c. When the optic axis is vertical?

5. What refractive index will a tetragonal crystal show under the following circumstances?

    a. When the *c* axis is horizontal and north-south.

    b. When the *c* axis is horizontal and east-west.

    c. When the *c* axis is vertical.

    d. When the *c* axis is north-south and inclined to the vertical.

    e. When the *c* axis is east-west and inclined to the vertical.

    f. When the *c* axis is horizontal and northwest-southeast.

    6. What refractive indices would be shown by the preceding if ordinary light were used instead of polarized light?

    ·7. Define the following terms: birefringence, pleochroism, optic axis, index ellipsoid, retardation, addition.

    8. An elongated crystal shows the following behavior when examined on the stage of a polarizing microscope: When north-south it is yellow, and when east-west it is orange, no analyzer being used. When the crystal is oriented northwest-southeast and the analyzer is pushed in, the crystal appears red and is turned orange by a selenite compensator and blue by a mica compensator. Give the pleochroic formula.

    9. A plate of quartz whose optic axis is horizontal and northwest-southeast shows an interference color corresponding to second-order orange. What is its thickness? (Look up indices.)

    10. A slide of uniaxial strontium chloride hexahydrate has indices 1.536 and 1.487. Given a slide of rod-shaped crystals mounted in Canada balsam (n 1.53), how would you establish that the vibration plane of the polarizer was north-south?

    11. Add to Table 18, Sec. 167, a column showing the type of interference figure given for each orientation. Note the utility of this table.

    12. The following laboratory data were recorded during an optical crystallographic study of an organic dye intermediate:

Appearance of crystals: (1) ▱ (2) △ . Colorless to faint yellow.
Figures: (1) Gives single isogyre that sweeps across field as stage is turned. (2) Gives centered cross and isochromatic curves. On introducing a quartz compensator whose slow ray vibrates northeast by southwest, the isochromatic curves move out in the northwest by southeast quadrant.
Extinction: (1) Symmetrical. (2) Dark in all positions.

    a. What is the crystal system and sign?

    b. Describe in a few sentences how you would measure the refractive indices.

    13. Look up and record the crystallographic properties and, if possible, the refractive indices and sign of

        a. $RbNO_3$.

        b. Tartaric acid.

        c. Diethylammonium chloroplatinate.

        d. $Na_6Be_6Si_{14}O_{37}$.

    14. A positive, pinacoidal, monoclinic crystal has the following properties: Optic plane = 010, $c \wedge \gamma = 10°$, $a \wedge c = 120°$.

    a. State the types of interference figure that might be shown when the crystal rests on 100, 001, 010.

    b. Give the character of extinction shown by crystals oriented as in *a*.

    c. Give the extinction angle to 100.

d. What refractive indices can be measured on crystals oriented as in *a*? Must these indices be measured at extinction positions?

15. *a.* What factors govern the number of isochromatic curves observed in a uniaxial optic-axis figure?

b. The statement has been made that the sign of elongation of a uniaxial crystal is always the same as the optic sign. Comment on this.

16. Small crystals of Dichrite show both parallel and isometric extinction. Those crystals which remain dark in all positions are eight-sided. Thin sections showing parallel extinction appear to be reddish gray and when placed with their optic axis northwest by southeast show almost no change in color upon introduction of a selenite or mica compensator. When a quartz-wedge compensator is used, however, the colors appear to move from the thin edges of the crystal toward the thicker interior parts of the crystal.

One of the crystals is set at extinction, and the analyser is removed. The crystal is yellow in this position and shows a high refractive index. When turned 90°, the color is green and the crystal shows a lower refractive index.

a. What is the crystal system?

b. What is the sign? Is the birefringence large or small? Give reasons.

c. Briefly explain the movement of the colors observed as the quartz wedge is introduced. Does the movement indicate compensation?

d. Is the extraordinary ray green or yellow?

17. An orthorhombic crystal has eight dome faces, four prism faces, and six pinacoid faces. The sign is positive, an optic axis makes an angle of 8° with crystallographic *c*, and crystallographic *a* is the optic normal. β is 1.500.

a. Sketch the crystal, naming each form (family of similar faces) and giving the Miller indices of each face.

b. Sketch the optical directions, showing their relationship to the crystallographic axes. Show both the optic angle and the apparent optic angle in the sketch.

c. If the crystal is lying on the 001 face, what refractive index may be measured when the optic plane is north-south? east-west? Repeat, assuming the crystal is lying on the 100 face.

18. A fragment of material shows oblique extinction and a centered acute bisectrix figure, the isogyres leaving the field of a N.A. 0.65 objective in 35° rotation. If the optic plane is placed northwest-southeast, compensation is observed on the specimen.

a. To what crystal system does the substance belong?

b. Is it (+) or (−)?

c. What is the orientation of the optic plane with reference to a pinacoid face?

d. What can you say about 2*E*?

e. What refractive indices can be determined on the fragment, and how will it be done?

19. A section of mineral cut parallel to a basal pinacoid shows parallel extinction and gives a centered flash figure, whose isogyres leave the extinc-

tion position in 16° rotation of the stage. A section parallel to 100 shows parallel extinction and gives a centered flash figure whose isogyres leave in 8° rotation. In both cases, when the optic direction that follows the isogyres is rotated into the northeast-southwest quadrants, compensation is observed on the specimen.

    a. What is the system?

    b. What is the sign?

    c. To what crystal face is the optic plane parallel?

    d. How do the α, β, γ vibration directions coincide with the *a*, *b*, *c* axes?

    e. What refractive indices are shown by a fragment lying on the 010 face?

    20. A positive monoclinic crystal shows forms as follows:

    4 unit prisms.

    2 orthopinacoids, 2 clinopinacoids, 2 basal pinacoids.

    a. Sketch the crystal, naming each form and giving Miller indices of each positive face.

    b. If $c \wedge Z = 10°$ and $b = Y$, what is the character of extinction when crystal is resting on 100, 010, 011, and 001 faces?

    21. A crystal lying flat on the stage of a polarizing microscope gives a centered interference figure. The figure consists of two hyperbolic brushes whose vertices lie on the edge of the field at their maximum separation. The central portions of the brushes are colored faintly blue. On slow clockwise rotation of the stage, the brushes move outward from the extinction position in the northeast and southwest quadrants. As the outward movement starts, the long direction of the crystal is north and south on the stage. The crystal is then turned so that it points northwest and southeast, the Bertrand lens and condenser are swung out, and a first-order red compensator is inserted. The crystal changes from yellow to white, and on 90° rotation, changes to blue. Under low magnification, a group of crystals oriented at random show only parallel extinction, with very bright colors.

    a. Draw all possible inferences as to the optical and geometrical attributes of the crystal.

    b. Construct a diagram of the optic orientation, naming all faces, axes, and optical directions, assuming the 100 face to be flat on the stage.

    22. Assume that you wish to characterize a crystalline compound that you have made. Your laboratory data are as follows: Some crystals appear as elongated rectangles showing parallel extinction, positive elongation, and inclined interference figures. Other crystals are short rectangles giving perfectly centered optic-axis figures with a single, sharply curved isogyre which is bluish on its convex side. When the convex side points northwest and a quartz wedge is inserted, the isochromatic curves move southeast. Most of the crystals are elongated rhombs with the acute angle equal to 40°. They show oblique extinction, the extinction angle being 30° (from longest edge) and give centered flash figures whose isogyres disappear very rapidly (10°). When the optic direction which follows the isogyres is placed northwest by southeast, compensation is observed on the specimen.

Characterization should include the items below. Indicate your reasoning.

   a. System and sign.

   b. Sketch of crystal and habit.

   c. Miller index of optic plane.

   d. Estimation of $2E$ and dispersion of the optic axes.

   e. Orientations of the crystal that will give the refractive indices (without use of figures).

   f. What is the relation of vibration directions to crystallographic axes?

   (Last item optional for extra credit.)

23. A monoclinic pinacoidal crystal resting on 010 is extinguished when the north-south cross hair makes an angle of 8° with the elongated *c* axis and gives a centered interference figure whose isogyres leave the field in 6° rotation of the stage. The crystal shows positive elongation when resting on any face. When resting on the basal pinacoid, a precisely centered optic-axis figure is seen. When the convex side of the gently curving isogyre is placed pointing northwest and a compensator inserted, the isochromatic curves move northwest. Measurement of the profile angle of the crystal when resting on 010 shows 001 $\wedge$ 100 = 40°.

   a. Make a rough sketch of the 010 profile showing the optic directions and optic axes in approximately their correct angular relations to the crystallographic axes.

   b. From the sketch and the preceding data, give the following crystallographic description of the crystal:

Sign = ? $c \wedge BXO$ = ?° $a \wedge BXA$ = ?° b = O.N. = ?° $2V$ = ?°

A brief statement of your reasoning should be included under each item.

REFERENCES

1. C. P. SAYLOR, *Bur. Standards J. Research*, **15**, 97 (1935).

2. F. EMICH (Schneider), "Microchemical Laboratory Manual," John Wiley & Sons, Inc., New York, 1935.

3. A. A. BENEDETTI-PICHLER, "Microtechnique of Inorganic Qualitative Analysis," Microchemical Service, Douglaston, N. Y., 1935.

4. F. EMICH, *Monatsh.*, **50**, 269 (1928); **53**, 312, **54**, 312 (1929).

5. R. C. EMMONS, *Am. Mineral*, **10**, 115 (1926); **13**, 504 (1928); **14**, 482 (1929).

6. A. N. WINCHELL, "Elements of Optical Mineralogy," Part I, John Wiley & Sons, Inc., New York, 1937.

7. M. J. BUERGER, *Am. Mineral.*, **18**, 325 (1933).

8. A. JOHANNSEN, "Manual of Petrographic Methods," McGraw-Hill Book Company, Inc., New York, 1932.

9. E. M. CHAMOT and C. W. MASON, "Handbook of Chemical Microscopy," John Wiley & Sons, Inc., New York, 1938.

10. V. L. BOSAZZA, *Am. Mineral.*, **25**, 299 (1940).

11. E. P. KAISER and W. PARRISH, *Ind. Eng. Chem. Anal. Ed.*, **11**, 560 (1939).

12. W. M. D. BRYANT, *J. Am. Chem. Soc.*, **55**, 3758 (1932).

13. V. F. HARRINGTON and M. J. BUERGER, *Am. Mineral.*, **16,** 45 (1931).
14. R. D. BUTLER, *Am. Mineral.*, **18,** 386 (1933).
15. A. H. KUNZ and J. SPULNIK, *Ind. Eng. Chem. Anal. Ed.*, **8,** 485 (1936).
16. B. W. ANDERSON and C. J. PAYNE, *Nature*, **133,** 66 (1934).
17. K. R. FOX and R. B. FINCH, *Textile Research*, **11,** 62 (1940).
18. J. K. ROBERTSON, "Introduction to Physical Optics," D. Van Nostrand,
    Company, Inc., New York, 1941.
19. W. SALOMON, *Z. Kryst.*, **26,** 178 (1896).
20. R. G. WOOD and S. H. AYLIFFE, *J. Sci. Inst.*, **12,** 194, 1935.
21. C. D. WEST, *J. Chem. Ed.*, **19,** 66, 1942.

CHAPTER VII

THE REFRACTOMETER

195. The refractive index of a transparent isotropic medium may be loosely defined as the "bending" power of the medium for a ray of light obliquely incident on its surface. This bending power is expressed precisely in the form of an equation

$$\frac{\sin i}{\sin r} = N_v$$

where i and r are the angles of incidence and refraction (Fig. 273) of a beam passing obliquely from a vacuum into the plane surface of the medium. For convenience, it is almost universal practice to refer to air as a standard for refractive indices rather than to vacuum. The refractive index relative to air is denoted by n and is related to N_v by the equation

$$\frac{N_v}{n} = N_{air} = 1.00027$$
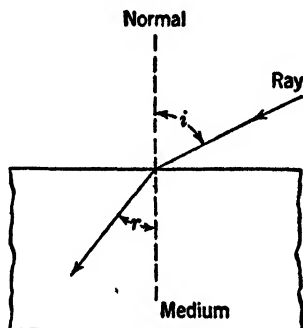
In general, the refractive index of a substance decreases with

FIG. 273.

increasing temperature and with increasing wave length of the illuminating ray. Because of this variation, it is necessary to specify these quantities and to adopt a conventional temperature and wave length for all measurements. Unless otherwise stated, the standard temperature is assumed to be 20°C. and the standard wave length 589 mμ (sodium D line). In certain specialized fields, other temperatures have become conventional, *e.g.*, 17.5°C. in sugar analysis, 25°C. for determination of edible oils, and 40°C. for fats, which are solid at room temperature. In view of the considerable change of refractive index with temperature, it is important to observe suitable precautions in controlling this

variable. Determination of the average temperature coefficient permits estimation of refractive index of liquids over a wide range of temperatures. This coefficient varies, of course, with the nature of the liquid, and in more precise work must be computed from a number of experimental determinations. The variation of refractive index with temperature is very nearly linear over a limited range.

TABLE 24.—WAVE LENGTHS COMMONLY EMPLOYED IN REFRACTOMETRY

Wave length, mμ	Symbol	Source	Color
589.6 (standard)....................	n_D	Sodium vapor	Yellow
656.3.............................	n_C or n_γ	Hydrogen	Red
486.1.............................	n_F or n_β	Hydrogen	Blue
434.0.............................	n_G or n_α	Hydrogen	Violet
546.1.............................	$n_{546.1}$	Mercury	Green

196. Partial dispersion is usually expressed as the difference in the observed refractive index of a substance for two different wave lengths of light. The wave lengths customarily chosen correspond to the hydrogen blue and red lines (Table 24), and the partial dispersion is expressed as $n_F - n_C$ or $n_\beta - n_\gamma$. A synthetic quantity called the nu value or Abbe number
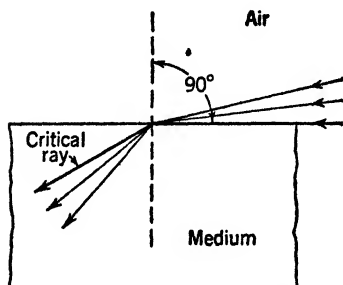
FIG. 274.—The critical ray.

$$\frac{n_D - 1}{n_F - n_C} = \nu$$

is much used to express dispersion because of its numerical advantages.[40]

197. The Concept of the Critical Angle.—When a ray of light just grazes the surface of a medium (Fig. 274), the angle of incidence is at its maximum value 90°. The refractive index is then determined solely by the angle of refraction of this so-called critical ray, since

$$n = \frac{\sin i}{\sin r_c} = \frac{\sin 90°}{\sin r_c} = \frac{1}{\sin r_c}$$

Obviously, if the critical angle may be measured, the refractive index may be calculated from this equation, or it might be

possible to graduate the measuring device directly in terms of
r or n. Measurement of the critical angle is not accomplished
directly but rather by means that will be illustrated in the next
few sections.

198. The Immersion Refractometer.—One of the simpler
critical-angle refractometers is the immersion or dipping refrac-
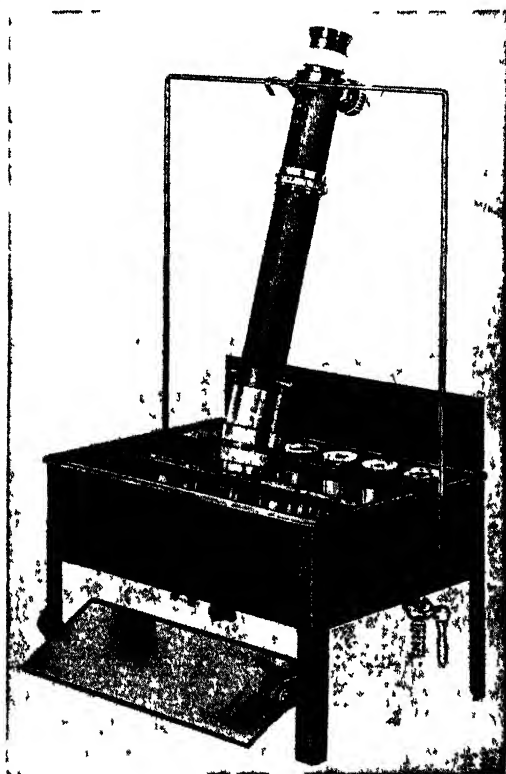
FIG 275 —Dipping refractometer or immersion refractometer. (*Courtesy of
Bausch & Lomb Optical Company.*)

tometer, which is capable of measuring the refractive index to
± 0.00003 (Fig. 275). Its working principle is illustrated in
simplified form by Figs. 276 and 277. Rays from a mirror pass
through a glass beaker containing the sample and enter the
special glass prism P (Fig. 276). The grazing or critical ray
forms the border line between the light and dark parts of the field
of view since no rays enter the prism at a greater angle. The
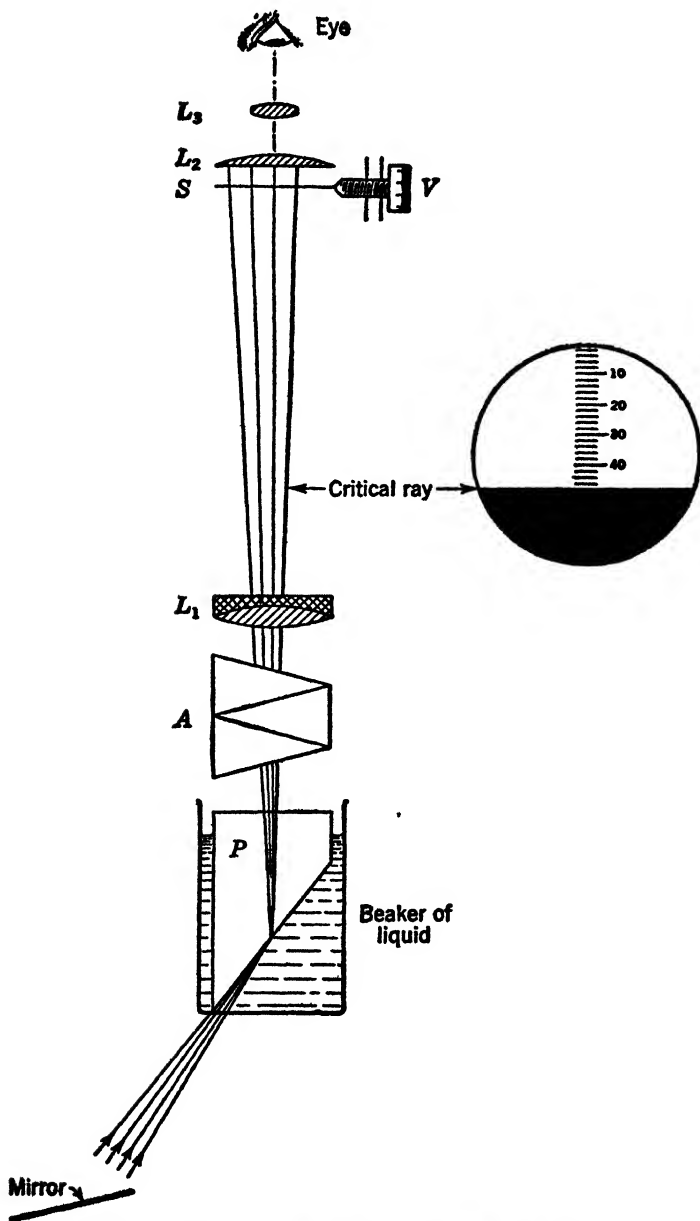
FIG. 276.—Simplified optical system of immersion refractometer.

optical parts of the instrument include the objective L_1 and the micrometer eyepiece L_2L_3. This latter is equipped with an accurately ruled scale and an ingenious vernier which permits estimation of the position of the dark border to a small fraction of a scale division. The Amici prism A is a triprism constructed from different varieties of glass and is so designed that it does not deviate a ray of light corresponding to the sodium D line. Rays of other wave lengths are deviated, however, and by rotating the Amici prism about the axis of the instrument, it is possible to just counteract the dispersion of light caused by refraction at the liquid interface. This important feature enables white light to be used for illumination and also permits estimation of partial dispersion by means of a graduated collar attached to the Amici

Fig .277.

prism. Further information of the construction and optics of the Amici compensator is given by Hardy and Perrin[1] and Dodd.[39]
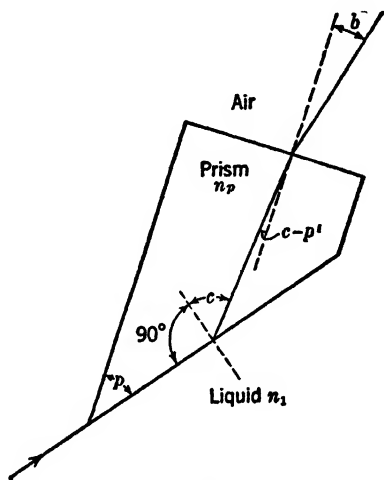
It is apparent from Fig. 277 that, in effect, the dipping refractometer is simply an instrument for measuring the critical angle c. The refractive index of the liquid is calculated by simple geometric relationships as follows: Let $p' = 90° - p$ then

$$\frac{n_l}{n_p} = \sin c = \sin [(c - p') + p']$$
$$= \sin (c - p') \cos p' + \cos (c - p') \sin p'$$
$$= \sin (c - p') \cos p' + \sin p' \sqrt{1 - \sin^2 (c - p')}$$

But

$$n_p = \frac{\sin b}{\sin (c - p')} \quad \text{or} \quad \sin (c - p') = \frac{\sin b}{n_p}$$

whence

$$n_l = \sin b \cos p' + \sin p' \sqrt{n_p^2 - \sin^2 b}$$
$$= \sin b \text{ const.} + \text{const.} \sqrt{\text{const.} - \sin^2 b}$$

Note that these relationships also hold for a transparent plane solid, placed in contact with the prism, as shown in Fig. 278.
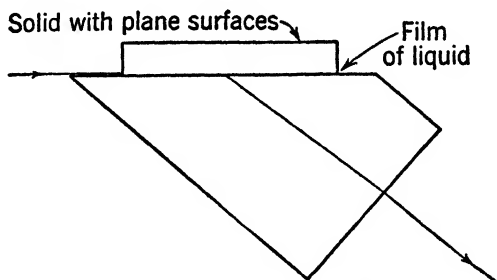
Fig. 278.—Position of immersion prism for measurements of solids.

In view of the difficulty of graduating a small transparent scale according to a sine distribution, the scale of the immersion refractometer is graduated in arbitrary equal units. A table for converting the scale reading to refractive-index units accompanies each instrument (Table 26).

TABLE 25.—REFRACTIVE INDEX OF WATER

Temperature, °C.	Refractive index	Temperature, °C.	Refractive index
18	1.3332	23	1.3327
19	1.3331	24	1.3326
20	1.33299	25	1 3325
21	1.3329	26	1.3324
22	1.3328	27	1.3323

199. Accessories for the Immersion Refractometer.—The range of refractive indices measurable with the immersion instrument is usually from about 1.32 to about 1.36. In some of the more recent models, a set of interchangeable prisms is available, which extends the range to about 1.5. These prisms must be calibrated by means of solutions of known refractive index or by means of glass test pieces which are placed directly on the prism face. A conversion table similar to Table 26 may then be used. .

For measurements on small quantities of liquids, an auxiliary wedge-shaped prism is provided. This prism is inserted in the beaker in such a way that its hypotenuse is parallel to the surface

Table 26.—Refractive Indices (n_D) Corresponding to Readings of
the Immersion Refractometer

(For Zeiss instruments, or Bausch and Lomb instruments whose serial number is over 10,000)

Scale reading		Scale reading		Scale reading		Scale reading		Scale reading	
0	1.32736	20	1.33513	40	1.34275	60	1.35021	80	1.35750
1	1.32775	21	1.33551	41	1.34313	61	1.35058	81	1.35786
2	1.32814	22	1.33590	42	1.34350	62	1.35095	82	1.35822
3	1.32854	23	1.33628	43	1.34388	63	1.35132	83	1.35858
4	1.32893	24	1.33667	44	1.34426	64	1.35169	84	1.35894
5	1.32932	25	1.33705	45	1.34463	65	1.35205	85	1.35930
6	1.32971	26	1.33743	46	1.34500	66	1.35242	86	1.35966
7	1.33010	27	1.33781	47	1.34537	67	1.35279	87	1.36002
8	1.33049	28	1.33820	48	1.34575	68	1.35316	88	1.36038
9	1.33087	29	1.33858	49	1.34612	69	1.35352	89	1.36074
10	1.33126	30	1.33896	50	1.34650	70	1.35388	90	1.36109
11	1.33165	31	1.33934	51	1.34687	71	1.35425	91	1.36145
12	1.33204	32	1.33972	52	1.34724	72	1.35461	92	1.36181
13	1.33242	33	1.34010	53	1.34761	73	1.35497	93	1.36217
14	1.33281	34	1.34048	54	1.34798	74	1.35533	94	1.36252
15	1.33320	35	1.34086	55	1.34836	75	1.35569	95	1.36287
16	1.33358	36	1.34124	56	1.34873	76	1.35606	96	1.36323
17	1.33397	37	1.34162	57	1.34910	77	1.35642	97	1.36359
18	1.33435	38	1.34199	58	1.34947	78	1.35678	98	1.36394
19	1.33474	39	1.34237	59	1.34984	79	1.35714	99	1.36429
								100	1.36464

of the immersion prism and separated from it by a thin film of the liquid to be examined. A single drop of liquid is sufficient.

Temperature control is secured through the use of a constant-temperature bath surrounding the beaker. To realize the maximum accuracy of which the immersion refractometer is capable, it is necessary to control the temperature of the liquid in the beaker to a tenth of a degree centigrade.

200. Experimental.—1. Examine the instrument and accessories. Place the clean dry prism in a beaker of distilled water, and mount the whole on the water bath. Adjust the temperature to 17.5°C., and maintain this temperature for 10 minutes..

The scale reading is then noted after adjusting the collar of the Amici compensator until the boundary is colorless and sharp. Use the vernier, and average five readings. Note the temperature after each reading. If the observed refractive index does not agree with that obtained from Tables 25 and 26 (scale should read 15.0 at 17.5°C.), the instrument may be adjusted according to the maker's directions (also see Browne[2]). If the instrument is not seriously in error, it is best to record a scale correction to be applied to subsequent readings.

After drying the prism with a soft cloth or absorbent tissue, make determinations on samples of Karo sirup diluted about 1 to 9 in distilled water. Determine the carbohydrate content and density by referring to Tables 3 and 8 in Browne.[2] What would be the effect of noncarbohydrate impurities?

2. Construct a graph of the refractive index of sodium chloride solutions vs. concentration or density.

3. Determine the temperature coefficient of water or some aqueous solution.

4. Determine total solids in egg white by the method of Almquist, Lorenz, and Burmeister.[3]

5. Determine the ethyl alcohol content of adulterated gasoline by the method of Mortimer and Giese.[4]

6. Determine adulteration of ethyl with methyl alcohol by the method given by Woodman;[5] see also Leach and Lythgoe.[6]

201. The Abbe Refractometer.—This instrument, which is probably more popular than any other type, is similar in principle to the immersion refractometer but is less accurate (± 0.0001). Its popularity is due to four factors: it reads refractive index directly, is durable, requires only a drop of sample, and gives a good approximation of partial dispersions. Some of the newer instruments possess the additional advantage that the refractive index of nearly opaque materials may also be measured.

The optics of the Abbe refractometer are practically the same as those already discussed in Sec. 198. As shown in Fig. 280, the illumination reflected from a mirror M passes into the illuminating prism P_i whose upper surface is rough ground. The rough surface acts as the source of an infinite number of rays which pass through the 0.1-mm. layer of liquid L in all directions. These rays then strike the surface of the polished prism P_r and are refracted. The maximum angle of refraction for these rays

is the critical angle, and, just as in the case of the immersion instrument, the critical ray forms the border between the light and the dark portions of the field viewed through the telescope which moves with scale S. The optical system includes the lenses L_1, L_2, and L_3; the Amici compensators A_1 and A_2, which may be rotated in opposition; and the cross hairs Ch in the focal
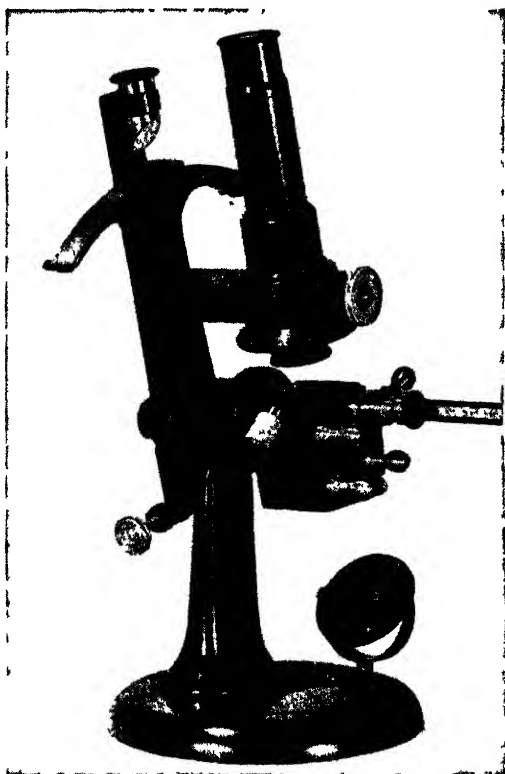
FIG. 279.—The Abbe refractometer. (*Courtesy of Bausch & Lomb Optical Company.*)

plane of the eyepiece. The prism mounting M revolves on a bearing and is rigidly connected to the arm B which moves the reading telescope RT over scale S, which is graduated directly for refractive-index measurement. The dispersion scale D graduated in arbitrary units, rotates with the Amici prisms.

202. Measurements with the Abbe Refractometer.—Determination of the refractive indices of liquids is described in
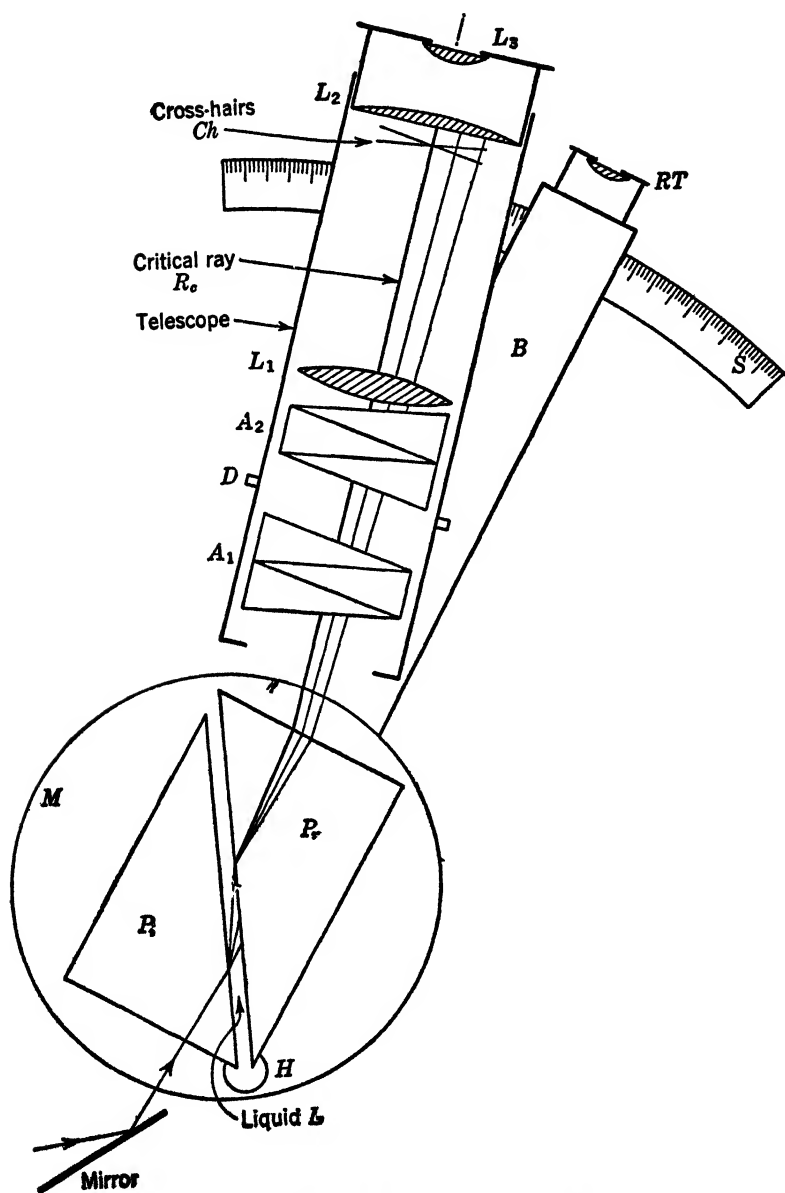
FIG. 280.—Simplified diagram of the Abbe refractometer.

Sec. 205. The measurement of the refractive index of solids, however, requires some explanation. By referring back to Sec. 198, it is easy to see that if the illuminating prism of the Abbe refractometer is swung out, the Abbe instrument conforms in principle to Fig. 278. If a plane-surfaced transparent solid material is then attached to the refracting prism by a thin film of a liquid *whose index is higher than that of the solid,* then the plane-surfaced solid determines the degree of refraction at the interface and the magnitude of the critical angle *c.* The purpose of the liquid of high index is to ensure optical contact between
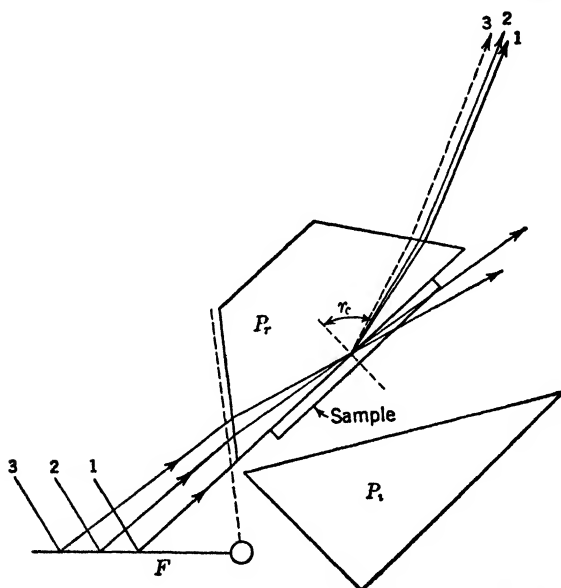
Fig. 281.—Trapezohedral prism for opaque solids.

the two solid surfaces. This being the case, it is obvious that the refractive index of solids may be measured either with the dipping or the Abbe refractometer.

An alternative method of measuring the refractive index of solids is applicable to nearly opaque materials and requires that the sample have only one plane surface. This method is likewise applicable to viscous opaque liquids such as tar or molasses. The device used for this method is incorporated in some of the more recent Abbe refractometers and is shown diagrammatically in Fig. 281. The illuminating prism P_i is swung out, and the

sample is placed in contact with the refracting prism P_r, which is trapezohedral in section. A hinged reflector F reflects rays into the sample prism interface as shown. The optical relations involved are similar to those already considered.

203. Temperature Control.—The necessity for close temperature control is not quite as critical for the Abbe refractometer because its accuracy is not so great as that of the immersion instrument. Control to at least $\pm 0.2°C$. is necessary however, and even closer control is desirable for liquids with a large temperature coefficient. The Abbe instrument is fitted with hollow prism casings, through which water may be passed, and a short thermometer is inserted into the jacket itself. Tap water is forced into a constant-level tower and then through a porcelain cylinder wound with resistance wire and provided with a sliding contact to regulate the amount of electric current. The water so heated flows through the prism casing of the refractometer and out to a drain.

Regulation of temperature by this means is very tedious unless the temperature of the tap water is constant. A much better method of control involves a simple thermostatic tank, of 10 liters or more capacity, and a small circulating pump. The only expensive part of this apparatus is the pump, which costs only about half as much as the conventional temperature-regulating equipment mentioned above.

204. Measurement of Dispersion.—The two Amici prisms of the Abbe refractometer are actually direct-vision spectroscopes so constructed that they deviate all wave lengths except that corresponding to the sodium D line. By rotating the two prisms in opposition, it is possible to cause their dispersion to cancel or to reinforce each other, or, in short, to attain any desired degree of dispersion. It is thus possible to cancel exactly the dispersion caused by the liquid when a sample is mounted for examination. The degree of rotation of the Amici prism necessary to counteract the dispersion of a liquid is a measure of the dispersion of the liquid. Although the Amici compensator scale is graduated in more or less arbitrary units, the maker of the instrument furnishes a graph that gives the dispersion or "nu value"

$$\frac{n_D - 1}{n_F - n_C}$$

as a function of n_D and the compensator reading.   The nu value may be estimated in some cases to about 5 per cent.   Dodd[39] gives a method of calibrating an Abbe refractometer for any wave length, which permits use of monochromatic sources for direct measurement of dispersion.   This method is considerably more precise than that described above.   Bielenberg[40] cites the utility of the nu value in ascertaining the constitution of organic liquids.

205. Experimental.—1. Examine the instrument carefully. Note the graduations of the two scales.   Both the field and reading telescopes may be focused.   (Why is the field black when there is no liquid between the prisms?)

Start the temperature-controlling device, and adjust to 20°C. Be sure that the prisms are clean and dry.   Introduce a drop of distilled water at the funnel-shaped opening between the prisms, or place a drop directly on the polished surface of the refracting prism, which is turned to a horizontal position.   Extreme care must be taken not to touch the prism surface with a dropping rod, since each contact, no matter how light, leaves a tiny pit in the soft, polished surface.

After introducing the sample, lock the prisms together and set the refractive index scale near 1.33.   The field will then show light and dark areas separated by a faint spectrum.   Adjust the light source and mirror, or tilt the whole instrument on its bearing so that the illumination is as bright as possible, then turn the knob of the Amici compensator until the dividing line between the halves of the field is sharp and free from color.   Move the arm carrying the reading telescope until the dividing line cuts the intersection of the cross hairs.   Read the refractive index, estimating the fourth place, and read the compensator scale. Make sure that the temperature has remained at 20°C. throughout.   Make five settings, and take the average.   Clean the prisms by gently wiping with a soft cloth or tissue.   Never leave the surface damp.   The instrument may be adjusted to the correct reading shown in Table 25 by a tiny screw near the compensator scale, or a numerical correction factor may be applied.   Find the dispersion from a chart supplied by the maker. For water at 20°C., $v = 55$.

2. As a further check on the accuracy of the instrument for higher indices, use the test piece supplied by the maker.   Place

a small drop of α-biomonaphthalene ($n = 1\ 658$) on the horizontal surface of the refracting prism, and press the test piece into place over this drop so that the piece is held without slipping The refractometer is then tilted on its bearing so that the test piece is illuminated by a near-by source or by light scattered from the surface of the pendant illuminating prism. The refractive index is read as for liquids   The prisms should be cleaned with alcohol.

Fig. 282.—The precision refractometer   (*Courtesy of Bausch & Lomb Optical Company*)

In accurate work at elevated temperatures, the effect of the decrease in refractive index of the prisms must be taken into account. The correction factor is best determined experimentally with a liquid of known temperature coefficient.

3. Determine the refractive index of a synthetic resin or plastic, referring to the tables given by West[7] and by Bradley.[8]

4. Determine the percentage fat in a sample of chocolate, using the method of Stanley.[9]

5. Determine the refractive indices of a piece of muscovite mica cut parallel to the extinction positions.   See the method of Record and Jones.[10]

6. Analyze a lacquer solvent by the method of Jenkins.[11]

206. The Abbe Precision Refractometer.—A modified Abbe instrument with a range of 1.40 to 1.70 or 1.33 to 1.50 and an accuracy of 0.00003 is described by Straat and Forrest.[12]   This instrument is similar to the Abbe in regard to the optical arrangement but has several additional features (Fig. 282).   The entire
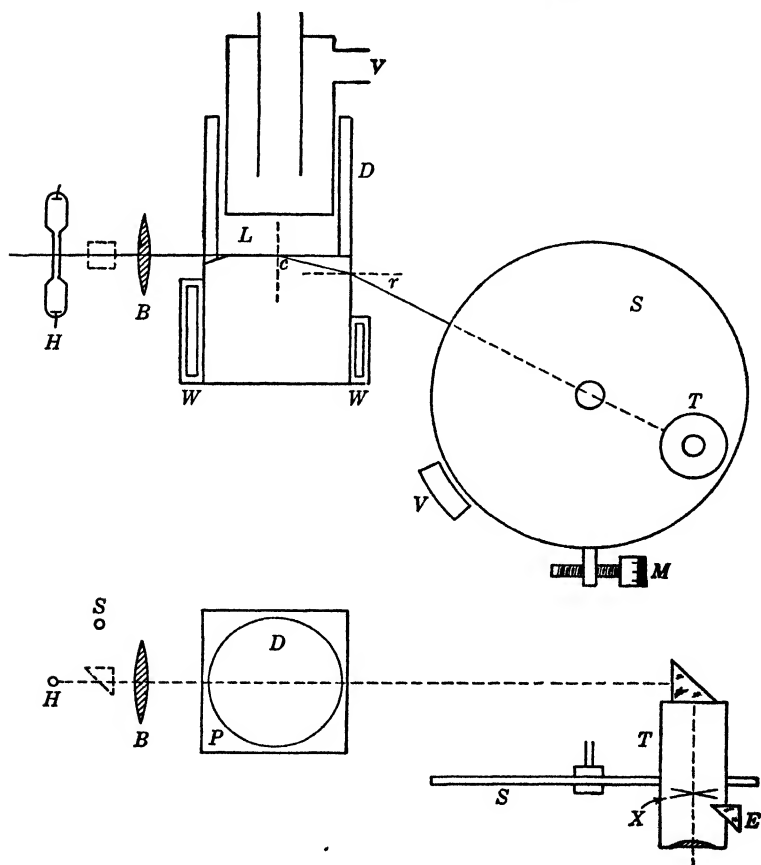
FIG. 283.—Simplified diagram of the Pulfrich refractometer.

instrument is mounted on a vertical bearing to eliminate flexing, and the Amici compensator is discarded in favor of an integrally mounted source of monochromatic illumination.

207. The Pulfrich refractometer is slightly more accurate than the Abbe but is considerably less convenient.   Its extensive use in research laboratories is due to its versatility and the precision of which it is capable in measurement of partial dis-

persions. A simplified schematic drawing is given in Fig. 283, where the cell D and prism P are enlarged out of proportion to the rest of the instrument. Light from a hydrogen discharge tube H, or from a sodium-vapor lamp S, is condensed by lens B and falls on the surface of the prism, which is covered with a layer of liquid L. A ray is refracted along the critical angle c and is again refracted on leaving the prism. Angle r is measured by means of the rotating circle S which carries the telescope T and cross hairs X. The vernier V is divided in half-degrees, whereas the micrometer drum M is graduated in $0.1°$ divisions. Temperature control is achieved through the use of an immersion tube and the hollow prism jacket W.

To calibrate the instrument, the zero point is first checked by means of the autocollimating prism E. Light from an outside source is directed through prism E and reflects from the surface of prism P. When the scale is set at $0°$, the cross hairs in telescope T should coincide with the image reflected from P. The refractive index of a liquid is then determined by measuring r and calculating the index by means of the equation

$$n = \sqrt{n_p{}^2 - \sin^2 r}$$

or from tables based on this equation. The accuracy is about ±0.0001. As scale S is rotated, the lines of the hydrogen spectrum will be visible in turn, and separate readings may be made for each line. Dispersions are measured by clamping the main scale and using the micrometer drum M which covers a range of only a few degrees.

The versatility of the Pulfrich instrument is due in part to the range covered and in part to the numerous interchangeable prisms available for special purposes, *viz.*, measurements on small and large amounts of sample, flow vessels for continuous measurements, and prisms for solid samples.

208. Other Refractometers.—Among the various types of refractometers designed for special purposes is the Féry auto-compensating instrument which is still used to some extent. This instrument, described at some length by Reilly and Rae,[13] has a range of 1.3000 to 1.6700 and an accuracy of ±0.0001. It requires 1 or 2 ml. of liquid sample and is neither so convenient as the Abbe nor so versatile. Monochromatic light is required, and dispersion is not measureable directly.

Several differential refractometers are in use; that of Amagat and Jeans[14] is used in oil analysis to compare the refractive
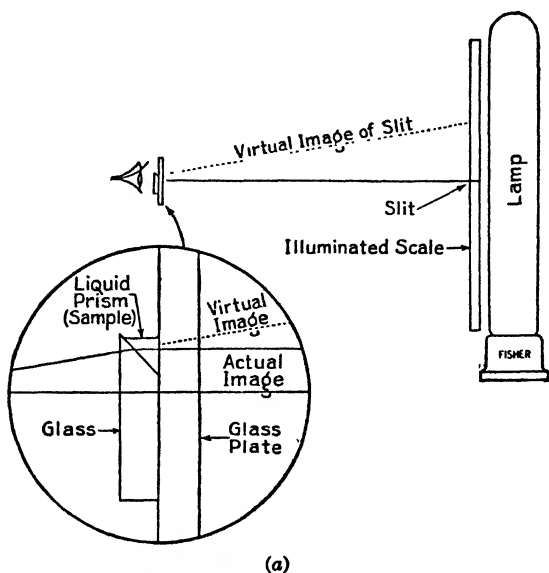
(a)

(b)

FIG. 284.—The Fisher refractometer.   (*Courtesy of Fisher Scientific Company.*)

indices of two oil samples.   Another device that is used for exceedingly accurate comparison of two samples is the Rayleigh interference refractometer.   The disadvantage of the latter is

the limited range, which is only about 0.01 units. Rau and Roseveare[15] have designed a very accurate type of refractometer operating on the differential principle of Ketteler.

The excellent device of Nichols has been described in Sec. 125. Other microrefractometers of similar design are described in the literature. One of the simplest is that of Jelley as described by Edwards and Otto,[16] who claim that it may be constructed for $4 and is accurate to ±0.3 per cent. An improved version of this instrument is made by the Fisher Scientific Company at a price well within the reach of any laboratory. The accuracy is said to be ±.001 (Fig. 284). Schroder[17] describes a method of determining refractive index by means of a cylindrical lens formed by a beaker containing the sample. Sheldon[18] describes a similar method involving a watch-glass lens. A more elaborate device is employed by Khan,[19] who determines the focal length of a concave mirror partly filled with the liquid in question. Jelley gives the design of a simple refractometer[20] made from a sextant and also describes an instrument[21] of different design.

Simms[41] determined refractive indices to 0.0005 by noting the apparent movement of a distant object viewed through a thin glass bulb containing the sample, which was suspended successively in a series of liquids of known index.

One of the simplest methods of determining index of refraction is the schlieren method mentioned in Sec. 159. A review of improvements in this technique is given by Taylor and Waldram[22] (see also Lamm[45]).

Wright[23] gives a list of 12 methods of determining the refractive index of drops.

209. The Refractive Index of Mixtures.—In cases where the volume of a mixture of two liquids equals the sum of the volumes of the components, it is possible to use the approximate equation

$$n = \frac{n_A v_A + n_B v_B}{v_A + v_B}$$

where v refers to volume. A related and more generally applicable version is given as

$$100 \left(\frac{n}{d}\right)_m = \frac{n_A \times \%A}{d_A} + \frac{n_B \times \%B}{d_B}$$

where d is the density and $\%$ refers to percentage by volume. (A more precise equation is given in Sec. 210.) Computations

for solutions that do not conform to these simple relations are reviewed in the "International Critical Tables," Vol. VII (see also Schwers,[24] Hubbard,[25] Glasstone,[26] and Cheveneau[14]). The latter gives an excellent review of refractometry as well as a complete discussion of the refractive index of solutions. De Lattre[43] disagrees with the equation of Schwers[24] and proposes an alternative relation. Merz[44] discusses practical aspects of the refractometry of mixtures.

210. The Use of Derived Constants Involving Refractive Index.—The utility of refractive index as a physical constant is greatly increased through the use of various derived or synthetic constants. These may be constants related directly to refractive index or they may involve dispersion. Table 27 gives the defining equations.

TABLE 27.—REFRACTIVE AND DISPERSIVE CONSTANTS

Name	Symbol	Definition	References
Refractivity	None	$n_D - 1$	
Specific refractivity	r_G	$\dfrac{n_D - 1}{d}$	30
Molecular refractivity	M_G	$MW \times r_G$	
Specific refraction	r_L	$\dfrac{n_D^2 - 1}{n_D^2 + 2} \times \dfrac{1}{d}$	31, 32, 27, 28
Molecular refraction	M	$MW \times r_L$	
Refractivity intercept	None	$n_D - \dfrac{d}{2}$	27, 28
Specific dispersion	None	$\dfrac{n_F - n_C}{d}$	29
Molecular dispersion	$M_C - M_G$	$M_C - M_G$	33
Specific refractive dispersion	Σ	$100(r_G - r_F)$	34, 25
Eykman constant	E	$\left(\dfrac{n^2 - 1}{n + 0.4}\right)\dfrac{1}{d}$	27

The Gladstone and Dale equation $(n - 1)/d = r_G$ is used to some extent in food analysis and other specialized fields where it is desirable to calculate approximate densities at various temperatures from refractive-index measurements. This is easily done if the value of r_G is known for the substance in question, since r_G is practically independent of temperature over a small range.

Specific Refraction $r_L = (n^2 - 1)/(n^2 + 2) \cdot 1/d$.—This equation, derived from theoretical considerations by Lorentz and

Lorenz, is a more accurate version of the Gladstone and Dale equation and is used for similar purposes. Although the theoretical derivation of this equation has been questioned,[36] it is capable of considerable accuracy. Its range of applicability is best illustrated by the fact that the approximate value of the refractive index of a vapor phase may sometimes be calculated from that of the liquid phase, and vice versa. This equation is likewise applicable to solids.

The molecular refraction M, obtained by multiplying r_L by the molecular weight of the refracting substance, is an additive constant much used in organic chemistry. The molecular refraction of a molecule is found to be very approximately equal to the sum of the atomic refractions of its component atoms or groups. The atomic refractions, so-called, are derived by noting the effect of adding groups to a parent molecule. Thus the constant difference observed in the molecular refractions of a series of homologous alkanes is due to the methylene group $>CH_2$. Table 28, which lists atomic refractivities, is modified from that of Roth and Eisenlohr.[37]

TABLE 28.—ATOMIC FACTORS FOR CALCULATING MOLECULAR REFRACTIONS

Group	M_G	M_D	M_F	M_C	$M_C - M_G$
I.....................	13.757	13.900	14.224	14.521	0.775
Br....................	8.803	8.865	8.999	9.152	0.340
S (mercaptan)..........	7.63	7.69	7.83	7.98	0.35
Cl....................	5.933	5.967	6.043	6.101	0.168
CN....................	5.434	5.459			
$>CH_2$................	4.598	4.618	4.668	4.710	0.113
N (tert. amine).........	2.807	2.840	2.940	3.000	0.186
N (sec. amine).........	2.475	2.499	2.561	2.603	0.119
C.....................	2.413	2.418	2.438	2.466	0.056
$C\equiv C$ (triple bond).....	2.328	2.398	2.506	2.538	0.171
N (pri. amine).........	2.309	2.322	2.368	2.397	0.086
O (carbonyl)...........	2.189	2.211	2.247	2.267	0.078
$C{=}C$ (double bond)....	1.686	1.733	1.824	1.893	0.200
O (ether)..............	1.639	1.643	1.649	1.662	0.019
O (hydroxyl)...........	1.522	1.525	1.531	1.541	0.015
H.....................	1.092	1.100	1.115	1.122	0.029

Not only does each atom have a characteristic additive effect, but in some cases the arrangement of the groups affects the observed molecular refractivity. Thus if two double bonds are

conjugated as in a diene —CH=CH—CH=CH—, the observable molecular refractivity and dispersion are greater than those calculated from Table 28.   This "exaltation" of refractivity is often useful as a test for the presence of a conjugated system. The exaltation is not observed, however, in a molecule such as benzene.   Further data on the effect of conjugation, ring formation, etc., may be found in Gilman[38] and Glasstone.[26]   The following calculations serve to illustrate some of the material discussed above.   The calculations are facilitated by tables of atomic refractivities $\times$ number of atoms and tables of the values of $\log (n^2 - 1)/(n^2 + 2)$ given by Roth and Eisenlohr.[37]

Example I

1,3-Dimethyl-1-allylcyclohexene-3

$MW = 150.14$	$11 \times C = 11 \times 2.418$	26.60
$d_4^{16} = 0.8415$	$18 \times H = 18 \times 1.100$	19.80
$n_D^{16} = 1.4729$	$2 \times C{=}C = 2 \times 1.733$	3.47
	M_r calc.	49.87

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = 50.4 = M_r \text{ obs.}$$

M_r obs. $- M_r$ calc. $= 0.53 =$ deviation
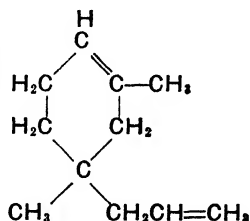
Example II

1,5-Dimethyl-3-isopropylidene cyclohexene-1
   (Isomeric with I)

$MW = 150.14$
$d_4^{22.5} = 0.8465$ M_r calc. $= 49.87$
$n_D^{22.5} = 1.4952$

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} = 51.75 = M_r \text{ obs.}$$

M_r obs. $- M_r$ calc. $= 1.88 =$ exaltation due
   to conjugation of the double bonds.
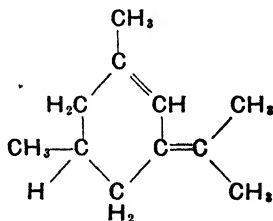
The molecular refraction of a mixture is given by the equation:

$$M_{1,2} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{x_1(MW)_1 + x_2(MW)_2}{d_{1,2}}$$

where (MW) represents the molecular weight and x the mol fraction.   Further, $M_{1,2} = x_1 M_1 + x_2 M_2$.   This equation permits determination of the molecular refraction of a solute in a solution of known concentration, and also permits determination of concentration as discussed in Sec. 209.

The refractivity intercept of Kurz and Ward is similar to the early Newtonian concept. The refractivity intercept is principally useful in petroleum chemistry for determining whether or not a given hydrocarbon belongs to a certain homologous series. The value of the intercept is characteristic *of the series.* Theoretically, the refractivity intercept is the refractive index of a hypothetical end member of the series having a density of zero, and it is obtained for any homologous series by extrapolating a curve of n vs. $d/2$ to the axis $d = 0$.

The utility of molecular dispersion and related constants lies principally in their use as additive constants (see Table 28). Specific dispersion and related constants are also useful in the analysis of hydrocarbons[29,42] and in ascertaining the constitution of organic liquids.[40]

The empirical Eykman equation is of value because it is relatively independent of temperature as compared with other refractive constants. None of these derived constants, however, is really valid in all cases and under all conditions.

PROBLEMS

1. What type of refractometer would you choose for the following? Make your answer in the form of a brief report to the head of a commercial laboratory. Look up prices if possible.

a. General use in a research laboratory.

b. General use in a plant.

c. Testing of dilute aqueous solutions when ample quantities are available.

d. Accurate measurement of dispersion for petroleum analysis.

e. Measurements on small quantities of volatile materials.

2. A laboratory is equipped with an accurate Bunsen spectrometer graduated in degrees and minutes. How would you modify it for use as a refractometer for liquids?

3. What factors influence the accuracy of an Abbe refractometer?

4. A solution of benzene ($n_D^{20} = 1.501$, $d_4^{20} = 0.879$) in absolute alcohol ($n_D^{20} = 1.361$, $d_4^{20} = 0.789$) has a refractive index of 1.395. What is the composition? What is the density?

5. A sugar solution is darkened by the presence of a minute amount of impurity so that its refractive index is not easily measureable. 14 g. of this sirup is diluted with an equal weight of pure sucrose solution containing 50 per cent sucrose. The resulting transparent mixture is found to have a refractive index of 1.4532 at 20°C. What is the percentage of sugar in the unknown sirup? (Consult Browne,[2] Table 5.)

6. Calculate the molecular refraction of the following compounds, and compare with the values calculated from n, d, and MW,
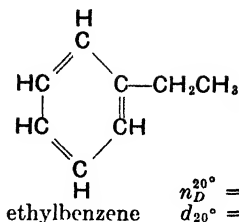
ethylbenzene $n_D^{20°} = 1.4959$
                 $d_{20°} = 0.8669$
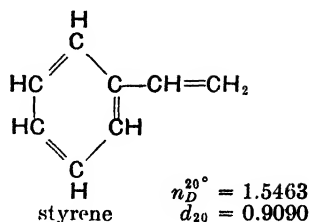
styrene $n_D^{20°} = 1.5463$
                 $d_{20} = 0.9090$

*7. Investigate the effect of 3, 4, 5, 6, 7, 8 membered rings on molecular refraction by calculating the values for isomers of ethylcyclohexane.

*8. Is $\log_{10} n/d$ an additive constant for a homologous series of aliphatic alcohols?

9. How many cubic centimeters of water could be detected refractometrically in 1 ml. of a supposedly dry sample of α-bromonapthalene ($n = 1.6580$) if the precision of the instrument is $\pm.00005$?

REFERENCES

1. A. C. HARDY and F. H. PERRIN, "The Principles of Optics," McGraw-Hill Book Company, Inc., New York, 1932.
2. C. A. BROWNE, "A Handbook of Sugar Analysis," John Wiley & Sons, Inc., New York, 1912. (See also Browne and Zerban, to be published 1941.)
3. H. J. ALMQUIST, F. W. LORENZ, and B. R. BURMEISTER, *Ind. Eng. Chem. Anal. Ed.*, **4**, 305 (1932).
4. F. S. MORTIMER and E. H. GIESE, *ibid.*, **5**, 356 (1933).
5. A. G. WOODMAN, "Food Analysis," McGraw-Hill Book Company, Inc., New York, 1940.
6. A. E. LEACH and H. C. LYTHGOE, *J. Am. Chem. Soc.*, **26**, 964 (1905).
7. C. D. WEST, *Ind. Eng. Chem. Anal. Ed.*, **10**, 627 (1938).
8. F. F. BRADLEY, *ibid.*, **3**, 304 (1931).
9. J. STANLEY, *Ind. Eng. Chem.*, **9**, 133 (1937).
10. F. RECORD and W. D. JONES, *J. Sci. Instruments*, **9**, 25 (1932).
11. J. D. JENKINS, *Ind. Eng. Chem. Anal. Ed.*, **2**, 127 (1930).
12. H. W. STRAAT and J. W. FORREST, *J. Optical Soc. Am.*, **27**, 240 (1939).
13. J. REILLY and W. N. RAE, "Physico-chemical Methods," Methuen & Co., Ltd., London, 1940.
14. C. CHEVENEAU, *Ann. chim. phys.*, **12**, 145, 289 (1907).
15. O. RAU and W. E. ROSEVEARE, *Ind. Eng. Chem. Anal. Ed.*, **8**, 72 (1936).
16. A. E. EDWARDS and C. E. OTTO, *ibid.*, **10**, 225 (1938).
17. J. SCHRODER, *Z. physik. Chem. Unterricht*, **23**, 26–8 (1910).
18. J. SHELDON, *J. Chem. Education*, **12**, 183 (1935).
19. M. A. R. KHAN, *J. Sci. Instruments*, **7**, 14 (1929).
20. E. E. JELLEY, *J. Roy. Microscop. Soc.*, **7**, 14 (1930).
21. E. E. JELLEY, *ibid.*, **54**, 234 (1934).
22. H. J. TAYLOR and J. M. WALDRAM, *J. Sci. Instruments*, **10**, 378 (1933).
23. F. E. WRIGHT, *J. Wash. Acad. Sci.*, **4**, 269 (1914).

* Indicates special problem.

24. F. Schwers, *J. Am. Chem. Soc.*, **101**, 1889 (1912).
25. J. C. Hubbard, *Z. physik. Chem.*, 74, 207 (1910); *Phys. Rev.* (I) **30**, 740 (1910).
26. S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Company, Inc., New York, 1940.
27. S. S. Kurtz and A. L. Ward, *J. Franklin Inst.*, **222**, 563 (1936).
28. S. S. Kurtz and A. L. Ward, *ibid.*, **224**, 583, 697 (1937).
29. A. L. Ward and W. H. Fulweiler, *Ind. Eng. Chem. Anal. Ed.*, **6**, 396 (1934).
30. J. H. Gladstone and T. P. Dale, *Trans. Roy. Soc. London*, **153**, 317 (1863).
31. H. A. Lorentz, *Wied. Ann.*, **9**, 641 (1880).
32. L. Lorenz, *ibid.*, **11**, 70 (1880).
33. E. Hückel, *Z. physik. Chem.*, **163**, 67 (1932).
34. K. Auwers and F. Eisenlohr, *Ber.*, **43**, 806 (1910).
35. T. M. Lowry and C. B. Allsopp, *Proc. Roy. Soc.* (*London*), series of papers (1937).
36. E. S. Larsen, *Am. J. Sci.*, **28**, 263 (1909).
37. W. A. Roth and F. Eisenlohr, "Refraktometrisches Hilfsbuch," Verlag von Veit, Leipzig, 1911.
38. H. Gilman, "Organic Chemistry—An Advance Treatise," Vol. II, John Wiley & Sons, Inc., New York, 1938.
39. L. E. Dodd, *Rev. Sci. Instruments*, **2**, 266 (1931).
40. W. Bielenberg, *Z. angew. Chem.*, **42**, 972 (1930).
41. H. S. Simms, *J. Ind. Eng. Chem.*, **13**, 546 (1921).
42. A. L. Ward and S. S. Kurtz, *Ind. Eng. Chem. Anal. Ed.*, **10**, 559 (1938).
43. G. De Lattre. *J. chim. phys.*, **24**, 289 (1927).
44. O. Merz, *Farben-Chem.*, **2**, 259 (1931).
45. T. Svedberg and K. O. Pedersen, "The Ultra-Centrifuge," The Clarendon Press, Oxford, 1940.

CHAPTER VIII

THE POLARISCOPE

211. Many liquids and solutions of liquids or solids are found to possess the power of rotating the vibration plane of polarized light. This rotatory power, or *optical activity*, is exhibited in in general by those liquids or solutes whose molecules do not possess elements of symmetry (Fig. 285). The magnitude and direction of the angular rotation suffered by polarized light in passing through a known thickness of liquid are of significance in the identification and quantitative estimation of optically active substances. Since the rudiments of the underlying theory of optical activity will be discussed in a later part of the chapter (Sec. 229), it suffices for the time being to regard the process as a rotation of the vibration plane of polarized light about the direction of propagation (Fig. 286).

The amount of this rotation depends upon the inherent rotating power of the substance and the following variables: the length of the column of liquid, the temperature, the wave length of the polarized light, and the concentration of the optically active substance, if a solute. In view of the effect of these variables, certain conventions are observed for the measurement of optical rotation, *viz.*, the wave length usually employed is either that of the sodium D line (5,893 A) or, less commonly, that of the mercury green line (5,461 A), and the temperature is conventionally 20°C. The specific rotation $[\alpha]_D^{20}$ of a solution is defined as the rotation in angular degrees which plane polarized light, corresponding in wave length to the sodium D line, undergoes in passing through a 1-dm. column of solution whose temperature is 20°C. and whose concentration is 1 g./cc. of solution. In mathematical symbols, this definition becomes

$$[\alpha]_D^{20} = \frac{av}{lw}$$

where a is the angular rotation, w is the weight of solute in v cc. of solution, and l is the length of the column of liquid in decimeters (10 cm.).

For pure liquids, the specific rotation is similarly defined as

$$[\alpha]_D^{20} = \frac{a}{ld}$$

where d is specific gravity at 20°C. referred to water at 4°C.

OPTICALLY ACTIVE   OPTICALLY INACTIVE

Bond permits free
rotation indicated
by arrows

• = H   ◯ = OH
• = C   ◉ = CH₂OH
⬤ = COOH
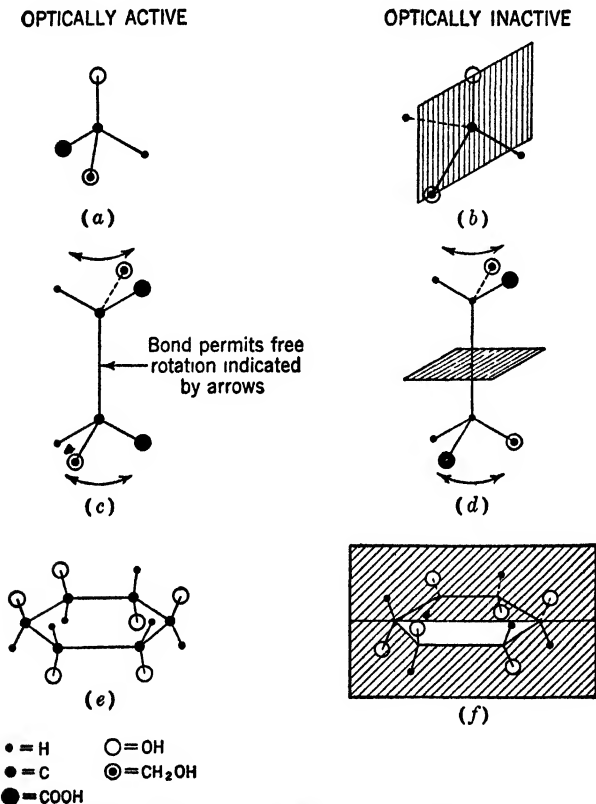
Fig. 285.—Optically active molecules do not possess a plane of symmetry (shaded plane). Note that the optically active molecule (*c*) cannot have a plane of symmetry no matter how the end groups are rotated, whereas the inactive isomer will have a plane of symmetry when the upper group is rotated a quarter turn to the left.

For solids, which also exhibit optical activity, the specific rotation is the rotation shown by a plate 1 mm. thick. Note particularly that the optical rotation of solids is not related to crystal anisotropy. For instance, isotropic sodium chlorate is optically active in the solid state, although it is inactive when dissolved.

Since the plane of vibration of polarized light may be rotated either clockwise or counterclockwise, it is necessary to observe a convention regarding the sign of rotation. If the rotation is
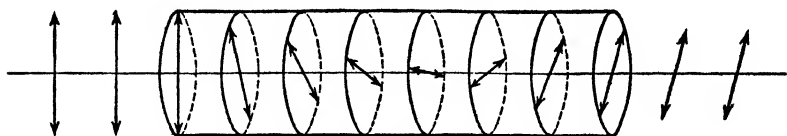
FIG. 286.

clockwise to an observer looking toward the light source, the rotation is said to be dextro, or $(+)$; if counterclockwise, the rotation is levo, or $(-)$.

THE POLARIMETER

212. Before elaborating upon the theories and calculations of polariscopy, it may be wise to deal with the actual measurement of optical rotation and the instruments employed for the purpose. The term *polariscope* is used to describe any instruments used for measurement of optical rotation. A *polarimeter* is generally a polariscope with a circular scale graduated in angular degrees, whereas a *saccharimeter* is a polariscope especially designed for sugar analysis, which may or may not have a circular scale and which is not usually graduated to read angular degrees.
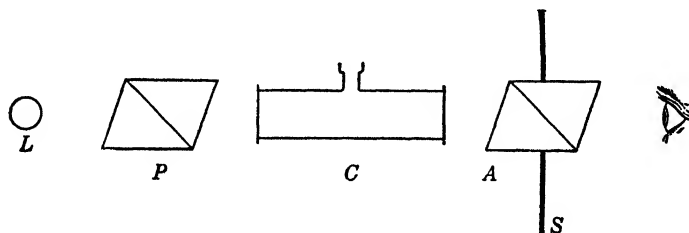
FIG. 287.—The simple polariscope.
L = source of illumination
P = polarizer
C = glass-windowed tubular cell
A = analyzer
S = rotary graduated scale attached to analyzer

The simple polarimeter is illustrated diagrammatically in Fig. 287. Light from source L is polarized by a fixed Nicol prism P and proceeds through the cell C, which for the moment will be considered empty. The analyzing Nicol A is now adjusted with reference to scale S so that when the two Nicols are "crossed"

the scale reads 0°. This point is, of course, ascertained by observing complete darkness in the field of view. If the cell is now filled with an optically active liquid, the vibration plane of the polarized light from the polarizer will be rotated so that the light reaching the analyzer will no longer be "crossed" with respect to the latter and will thus be transmitted (see Sec. 165). The amount by which the analyzer must be rotated to restore the point of darkness, or "endpoint," will, of course, be equal to and in the same direction as the rotation caused by the liquid and may be read on the scale S in terms of angular degrees.

213. Why Monochromatic Light Is Necessary.—In the foregoing description, no mention was made of the nature of the illumination from source L. This illumination must be strictly monochromatic, and source L is usually a sodium flame or sodium-vapor lamp whose rays are filtered through a suitable filter. The reason for using monochromatic light becomes apparent when we consider that different wave lengths of polarized light may be rotated different amounts by an optically active material. In fact, this difference in rotation may be quite large, as illustrated in Table 29, for a cholesterol solution.

TABLE 29.—EFFECT OF WAVE LENGTH ON ROTATION OF CHOLESTEROL

Wave length	$[\alpha]^{20}$	Relative values
686.7	−20 63	1.00
656.2	−25.54	1.24
589.3	−31.59	1.53
526.9	−39.91	1.93
486.1	−48.65	2.36
430.7	−62.37	3 02

The effect of using white light as a source is interesting since on rotating the analyzer one obtains, instead of an end point, a series of colors complementary to whatever colors are cut out by the analyzer. Thus, if the vibration plane of the analyzer is perpendicular to the vibration plane of red polarized light, red will be cut out of the spectrum and the field of view will appear blue-green, etc.

214. End-point Devices.—One of the obvious faults in the above-mentioned simple polariscope is the difficulty of determining the precise end point, or point of maximum darkness.

Although the eye is an exceedingly poor judge of absolute intensities, it is capable of matching the intensities of two simultaneously viewed fields with great accuracy. For this reason, all polariscopes intended for serious work are equipped with an optical device that splits the field into two or more adjacent parts such that when the end point is reached the sections of the field become of the same intensity. A very slight rotation of the analyzer will then cause one part to become darker and the other lighter. The increase in sensitivity so attained is best emphasized by the fact that a maximum accuracy of better than $\pm 0.01°$ is readily attained through the use of an end-point device, whereas the unaided eye cannot make settings to better than perhaps ± 4 or $5°$. Several types of end-point devices will be discussed in the following paragraphs.

The Jellet-Cornu Split Prism.—This end-point device is constructed from a ¦Nicol prism by cutting it in two along the optic axial plane (Sec. 165), removing equal wedge-shaped sections, and then cementing the halves together again. This construction is shown in Fig. 288, where the arrows represent vibration directions.

Fig. 288.—Construction of split prism from Nicol prism. (Arrows indicate vibration directions.)

The split prism is used in place of a polarizer and produces, instead of a single ray of polarized light, two rays whose vibration directions PP and PP' (Fig. 289) make a small angle, usually about $5°$. The effect of this condition is shown in Fig. 289, where AA' represents the vibration plane of the analyzer. When the latter makes equal angles with the two polarized rays from the split prism, the two halves of the field will be of equal intensity. A very slight rotation of the analyzer in either direction causes an easily discernible change in the relative intensities.

The Lippich end-point device achieves the same result as the split prism, but the two polarized rays are produced by means

of two Nicol or other polarizing prisms mounted as shown in Fig. 290. The small Nicol covers half the field of the large polarizer, and its optic plane is rotated slightly with respect to that of the polarizer. The vibration planes of the two rays of polarized light so produced are indicated by the arrows shown in the drawing. It should be observed that since these two rays are not of exactly the same intensity the end point will not be that point (Fig. 289) at which the vibration plane of the analyzer makes equal angles with the two vibration planes of the two rays. This is immaterial, of course, in practice. Note
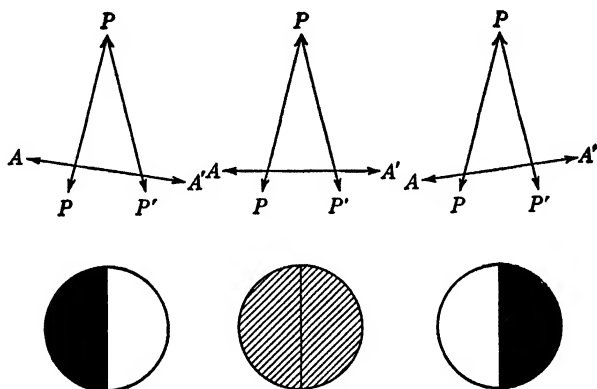
End-point
Fig. 289.

that the angle between the vibration planes of the two rays may be altered by a slight rotation of the polarizer.

The introduction of another small prism into the Lippich device greatly increases its accuracy. The three prisms of the "triple-field polarizer" are arranged so that the field of view is divided in three equal parts. The outer portions receive light from the small prisms, whose vibration planes are parallel. The end point is marked by a match of intensities in the three parts of the field.

The Laurent half-wave plate is an end-point device whose working principle is similar to but rather more complicated than the foregoing. It is a plate of quartz cut parallel to its optic axis (Chap. VI) and of such a thickness that its slow ray lags exactly one-half wave length behind the fast ray, for light corresponding to the sodium D line. This plate is placed between the polarizer and the cell so that it covers just half the face of the polarizer,

the other half being covered by a plate of glass. In Fig. 291, let *OP* represent the vibration plane of polarized light from the polarizer *N*. Part of this light goes directly to the analyzer, but part is intercepted by the quartz plate, which resolves it into two vibration directions *OC* and *OB*. During passage through the plate, ray *OB* becomes half a wave length (180°) out of phase with ray *OC* and emerges from the plate as *OD*. Rays *OC* and *OD* may be considered as equivalent to their resultant *OR*, which assumption permits comparison with the preceding end-point devices. When the vibration plane of the analyzer makes equal angles with *OR* and *OP*, the field is uniformly
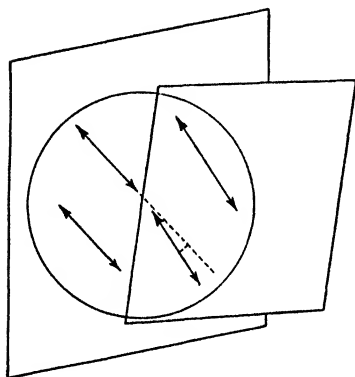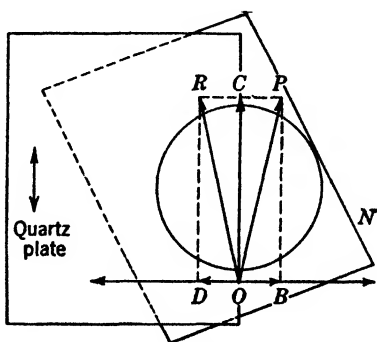
FIG. 290.   FIG. 291.

FIG. 290.—Front view of the Lippich polarizer. (Arrows indicate vibration directions. The circle represents the field of view and the edge of the smaller Nicol prism is the dividing line between the two halves of the field.)

FIG. 291.—The Laurent end-point device.

illumined. Note that the dividing line between the two halves of the field is the edge of the half-wave plate and, further, that by rotating the polarizer the angle *ROP* may be altered at will without changing the zero point of the instrument.

This latter feature is of great importance since the sensitivity of the end point varies inversely with the size of the half-shadow angle. Thus, when angle *ROP* is small, a very slight rotation of the analyzer from the zero setting will cause its vibration plane to become nearly crossed with respect to one of the rays from the polarizer with the result that one-half of the field becomes nearly black. If the angle *ROP* were larger, a greater rotation of the analyzer would be necessary to produce the same effect, *i.e.*, the

device would be less sensitive. Note, however, that the larger the half-shadow angle, the brighter will be the field at the end point. This condition is often desirable when highly colored liquids are under investigation.

TABLE 30.—COMPARISON OF END-POINT DEVICES

End-point device	Advantages	Disadvantages
Split prism..... ..	Rugged construction May be used in saccha- rimeter (Sec. 217)	Invariable sensitivity
Lippich.........	Most sensitive May be used in saccha- rimeter Variable sensitivity	End point changes as sen- sitivity is altered Fragile construction, edge of small prism becoming etched in time
Laurent.........	Variable sensitivity with no change in end point	Used for sodium D light only

215. The Construction of the Polarimeter-Accessories.—Several types of standard polarimeters are available, and excellent descriptions are to be found in most texts on sugar analysis, notably Browne.[1] The essential features of a standard polarimeter are shown in Fig. 292, with its accompanying description. For approximate work, a simple and inexpensive polarimeter utilizing Polaroid is now available (Spencer Lens Co.[21]).

Polarimeter accessories include a set of observation tubes (Fig. 293), preferably of the side-opening type, 1, 2, 2.2, or 4 dm. in length. A water-jacketed tube for close temperature control is often desirable, and a micro tube with a capacity of a fraction of a cubic centimeter is exceedingly useful when only minute amounts of sample are available.

A convenient method of checking the accuracy of the polarimeter is provided by a control plate of optically active quartz, whose rotation has been checked by the Bureau of Standards.

✓**216. Monochromatic Sources.**—Two sources of illumination are more or less standard in polarimetry: the sodium flame or vapor arc and the filtered mercury arc. In either case, it is necessary to employ filters to remove unwanted wave lengths, since the purity of the illumination is very important. The
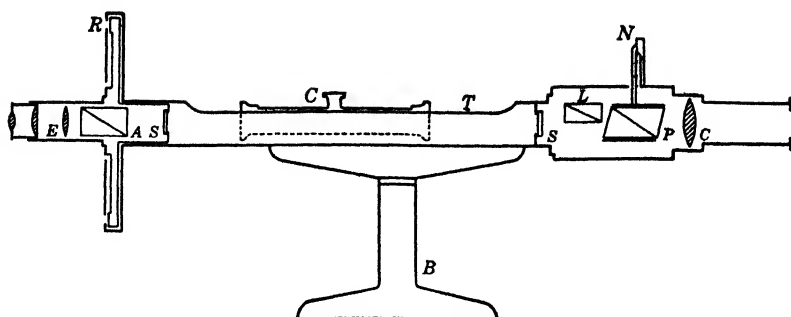
FIG. 292.—The polarimeter (schematic).

E = eyepiece
A = analyzer
SS = splash plates
R = circular scale (enclosed)
C = polariscope tube
T = trough (shown without cover)
L = Lippich prism
P = polarizer
N = half-shadow setting
C = collimator
B = support stand
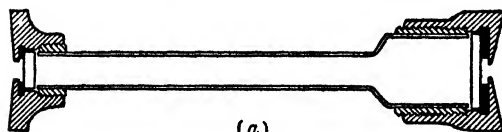
(a)
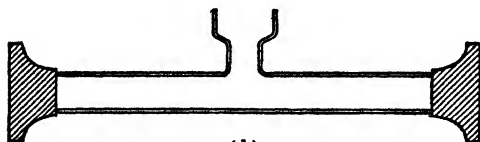
(b)
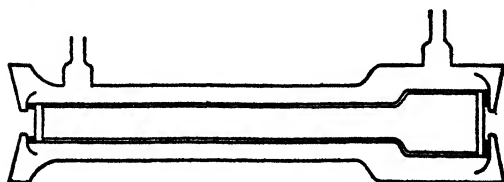
(c)

FIG. 293.—Polariscope tubes: (a) common type; (b) side opening; (c) jacketed.

most commonly used filter for the sodium lamp is a 1.0-cm. cell filled with 9 per cent aqueous potassium bichromate or an equivalent solid filter. Standard glass filters are available for isolating the green mercury line (see Sec. 117). Further data on filters, sources, and monochromators may be found in any standard work on polarimetry[2,3] (see also a review by Bates[4]).

Whatever the source employed, it is desirable to place it in such a position that the condensing lens of the polariscope forms an image just in front of the analyzer, *i.e.*, at the analyzer diaphragm (on the side toward the polarizer). If a sodium flame is used, it should not be placed too close to the condensing lens of the instrument.

Polariscopes are generally set up in a large case provided with a small opening at one end, through which the condenser projects, and a door at the opposite end. The cover should be hinged, and the entire box should be blackened inside with "optical black." The polariscope room must be partly darkened so that there are no bright areas visible to the operator. If the instrument is not equipped with a built-in illuminator for the scale (Fig. 295), a small lamp is easily improvised from a 4-watt bulb and a metal shield, or a small mirror may be employed to reflect light from the sodium lamp onto the scale. No extraneous light must enter the eye of the operator.

THE SACCHARIMETER

217. The polariscopes so far discussed all suffer from one great disadvantage, *i.e.*, they all require monochromatic illumination. This defect becomes really serious when colored or cloudy solutions are to be studied, since the usual sources of monochromatic light are not sufficiently intense. Obviously, an instrument that could be used with white light would be a great improvement in this respect and would also be more portable for field work. The quartz-wedge saccharimeter described below possesses just these advantages, but unfortunately it may be used only for analysis of solutions of cane sugar and a few related substances.

Theory of the Quartz-wedge Compensator.—From Sec. **213**, it appears that the necessity for monochromatic light in polarimetry arises from the fact that different wave lengths of polarized light are rotated different amounts by an optically active material.

It therefore follows that in order to eliminate this rotatory dispersion it must be neutralized by a medium possessing a *similar but opposed* rotatory dispersion. Such a medium is found in crystalline levo quartz cut so that light passes through it along the optic axis. It is found that a plate of levo quartz does in fact show rotatory dispersion of almost precisely the same type as solutions of cane sugar and that this dispersion is in the opposite sense. In other words, if a plate of quartz is of such a thickness that it neutralizes the rotation of a sugar solution for one wave length, then it also neutralizes the rotations for all other wave lengths. This fortunate circumstance serves as the working
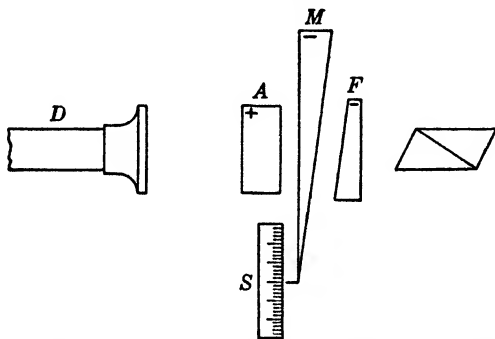
Fig. 294.—The quartz-wedge compensator (schematic).

principle of the Soleil quartz-wedge compensator shown in Fig. 294. Polarized white light from the polarizer enters the dextro (+) rotating quartz plate A and proceeds to the combination levo (−) quartz-wedge system MF where M is a movable wedge attached to a linear scale S. The thickness of the system MF is adjusted so that its levo rotation just equals the dextro rotation of A when the scale S reads zero. If now a sucrose solution is placed in cell D, the increase in total dextro rotation thereby produced is canceled by increasing the thickness of the levo system MF. Since the thickness of levo quartz necessary to just cancel the rotation and dispersion of the solution is proportional to the rotation of the solution, the scale S may be graduated to read rotations directly. Owing to the similarity of the rotational dispersions of quartz and sucrose solutions, the dispersion of the latter is also canceled by the levo wedge system and the end-point field is free from color. Lippich and Jellet-Cornu end-point devices are commonly used, since the Laurent

PLAN VIEW OF PATH OF LIGHT & OBSERVATION TUBE SHOWN TWICE SIZE OF VIEW BELOW

Path of Light
through
Half-Shadow
Saccharimeter

F—Polarizer
G—Splash Glass
H—Observation Tube
II—Quartz Compensator
J—Analyzer
K—Observing Telescope
L—Scale Illuminating Prism
M—Condensing Lens
N—Scale and Vernier Plates
O—Scale Reading Eyepiece
P—Glass Filter in Scale Illuminating System
O—Photometric Field as seen from Eyepoint

1—Plane of Polarization
    of Analyzer
2—Planes of Polarization
    of Semi-Fields
3—Half Shade Angle
A—Light Source
B—Ground Glass Lamp Window
C—Cover Glass
D—Glass Filter Replacing Bi-
    chromatic Cell
E—Condensing Lens

FIG. 295.—(Courtesy of Bausch & Lomb Optical Company.)

plate is not suitable for use with white light. Naturally, it will be impossible to obtain clear end points in the case of a liquid whose rotational dispersion is not similar to that of quartz. If the difference is only slight, however, as is the case with most sugar solutions (dextrose, etc.), a fairly sharp end point may be obtained through the use of a yellow filter placed in front of the polarizer. A 1.5-cm. column of 6 per cent potassium bichromate, or 1.0-cm. column of 9 per cent potassium bichromate is used for this purpose.

A standard saccharimeter made by the Bausch & Lomb Optical Company is shown in Fig. 295. For descriptions of other types, see Browne,[1] Lowry,[5] and Rolfe.[6] Attention should be called to the many modifications of the simple quartz wedge described above, e.g., the double-wedge compensator used in certain of the Schmidt and Haensch instruments (Fig. 296).
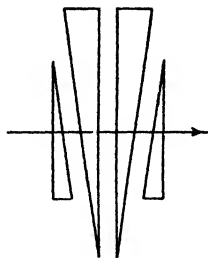
FIG. 296.—Double-wedge compensator.

COMPUTATIONS OF POLARIMETRY

218. The definition of specific rotation given at the beginning of the chapter provides the means of calculating the specific rotation from the observed rotation, concentration, and tube length. For the sake of convenience, the symbols and equations most frequently employed are listed below.

a = observed rotation in degrees.

$[\alpha]_\lambda^t$ = specific rotation at temperature t.

l = tube length, dm.

d_4° = specific gravity, referred to water at 4°.

c = concentration of solute, g./cc. of solution.

p = concentration of solute, g./100 g. of solution = %.

$[M]_\lambda^t$ = molecular rotation = $\dfrac{[\alpha] \times (MW)}{100}$.

w = weight of solute, g.

v = volume of solution, cc.

$[\alpha] = \dfrac{a}{l}$ for solids where l is in millimeters.

$[\alpha] = \dfrac{a}{ld}$ for pure liquids where l is in decimeters.

$[\alpha] = \dfrac{a}{lc} = \dfrac{av}{lw} = \dfrac{100a}{lpd}$ for solutions.

219. Variation of Specific Rotation with Concentration.—
The specific rotation of solutions of most optically active materials is dependent to a greater or lesser extent on the concentration of the solution and also upon the nature of the solvent. In the majority of cases, this variation is small, but it must always be taken into account in determining specific rotation.

The relation of $[\alpha]$ to concentration is best considered in the form of a graph such as that shown in Fig. 297, where the y axis represents specific rotation and the x axis represents the percentage of *solvent* in the solution. Note that the specific rotation may either increase or decrease with increasing concentration and that the relation may or may not be linear.
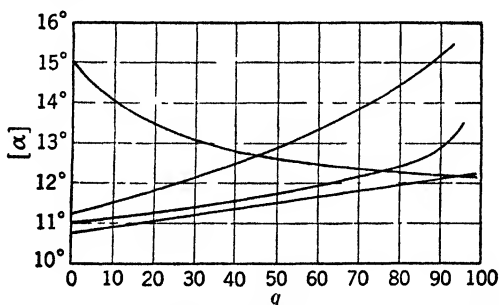
Fig. 297.—Four of the many ways in which $[\alpha]$ may vary with the concentration.

Three possible curves of $[\alpha]$ vs. concentration are expressed mathematically in the three equations of Biot:

$$[\alpha] = A + Bq \text{ (straight line)}$$
$$[\alpha] = A + Bq + Cq^2 \text{ (parabola)}$$
$$[\alpha] = A + \frac{Bq}{C + q} \text{ (hyperbola)}$$

where $[\alpha]$ is the observed specific rotation, A and B are constants, and q is the percentage of solvent in the solution $(100 - p)$. It is usually possible to fit one or the other of these equations to the experimental data, and the values of the constants may be calculated by the method of least squares. For the present purposes, we shall discuss only the simple linear relationship which is almost always applicable over a small range for solutions of high concentration.

On consideration of the linear Biot equation, it appears that when the percentage of solvent q is zero then $[\alpha] = A$. But if

the percentage of solvent is zero, then the solute must be in undiluted form and the value of $[\alpha]$ that equals the constant A in the equation must be the specific rotation of the pure solute. Because of the fact that the specific rotation of pure liquids equals a/ld, it is usual to express the values of $[\alpha]$ in the Biot equation as a/lpd, the volume term being omitted.

A sample calculation illustrates the procedure used to calculate the specific rotation of a pure liquid from data obtained from solutions.

Solution	p	q	d_4^{20}	a (in 2-dm. tube), deg.	$[\alpha]_D^{20}$, deg.
1	73.09	26.91	0.8765	+20.42	+15.94
2	47.51	52.49	0.8464	+13.08	+16.26
3	22.24	77.76	0.8186	+ 6.04	+16.59

On plotting $[\alpha]$ against q, a straight line is obtained indicating that the simple equation $[\alpha] = A + Bq$ may be used. Substituting the preceding values, we have

(1) $15.94 = A + 26.91B$
(2) $16.26 = A + 52.49B$
(3) $16.59 = A + 77.76B$

Solving (1) and (2), (2) and (3), or (1) and (3) simultaneously, it is found that $B_{avg} = 0.01290$ and $A = +15.62°$, which is the specific rotation of the pure solute.

If the solute happens to be a solid substance, the physical significance of A is not entirely clear, but it may be considered as the specific rotation of the solid in a glassy, noncrystalline state. It is important not to confuse this rotation with the rotation of the crystalline material which is due not to the molecules themselves but to the supposedly helicoidal crystalline structure.

Landolt,[7] who discusses the effect of concentration in more detail, cites four conclusions which, in simplified form, are as follows:

1. The specific rotation of a substance undergoes a progressive change as an inert diluent is added.

2. The specific rotation of a pure solute may be calculated from measurements on solutions.

3. The value of the specific rotation thus computed is the same for all inert solvents.

4. The value thus computed is the only value that may be used for comparing the rotations of solutions of different substances.

220. The effect of the solvent on the observed rotation of a solution may be relatively slight or it may be as profound as in the case of methyl-1-methylnaphthalate, whose molecular rotation varies over a range of 500° in different solvents.

The physical reasons for such variations are complex, and their discussion is beyond the province of a text on analytical chemistry. Complete discussions are given by Rule[8] in a series of articles. It suffices here to state that the effect of the solvent depends to a large extent on its polar nature as compared with that of the solute. In nonpolar solvents, a high concentration of polar solute favors association of solute molecules, with a resulting decrease in rotation. In solutions where they are in effect completely dissociated, the optical activity of electrolytes is independent of the inactive ion. Thus all salts of an optically active base should have very nearly the same rotation per gram equivalent, irrespective of the acid radical.

Recent work has shown that the presence of foreign materials such as urea, inorganic salts, and amino acids, has an appreciable effect on observed rotations. No general rule may as yet be given for such anomalous effects (see Browne[1]). Turbidity must be entirely absent.[19]

221. The Effect of Temperature.—When an observation tube containing an optically active liquid or solution is heated, three effects must be taken into account. The most obvious of these is the effect of expansion of the tube which tends to increase the rotation. The second effect is the attending decrease in density on heating, which reduces the number of optically active molecules per unit length. The third effect is that of temperature acting upon the molecules themselves and their tendency to associate, etc. No general rules can be given except that the reason for variation with temperature is probably the increased mobility of the groups attached to the asymmetric carbon which results in possible changes in configuration.

Substances vary greatly in their temperature coefficients of rotation. For instance, the change shown by sucrose is rather

small, whereas that of d-fructose is unusually large. The effect is usually expressed as an equation

$$[\alpha]_D^t = [\alpha]_D^0 + nt$$

where n is the temperature coefficient and t is the temperature in centigrade degrees. For fructose $n = 0.32$, and for sucrose $n = 0.0144$. The rotation of invert sugar, which is composed of equimolar amounts of dextrose ($[\alpha]_D^{20} = +52.5°$), and d-fructose ($[\alpha]_D^{20} = -93°$), becomes zero at 87.2°C., owing to the reduction of the rotation of d-fructose. This fact is used in the determination of invert sugar (Sec. 228).

222. The Effect of Wave Length—Rotational Dispersion.— This topic has been touched on briefly in Sec. 213, but it is of such importance in theoretical chemistry that it deserves further mention.

In general, the variation of specific rotation with wave length may be expressed by a single- or poly-term Drude[9] equation:

$$[\alpha] = \frac{k}{\lambda^2 - \lambda_0^2} \qquad \text{or} \qquad [\alpha] = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} + \frac{k_3}{\lambda^2 - \lambda_3^2} \cdots$$

where $[\alpha]$ is the specific rotation, or more commonly, the molecular rotation, k, k_1, etc., are constants, and λ_0, λ_1, etc. are also constants, although the latter have true physical significance in that they represent approximately the wave lengths of the heads of absorption bands (see Chap. II). Those substances whose dispersion may be predicted by the single-term Drude equation are said to have simple rotatory dispersion, whereas if two or more terms are required, the dispersion is said to be complex. If a graph of $[\alpha]$ vs. λ shows a minimum, maximum, or point of inflection, the dispersion is termed anomalous. In the latter case, the sign of one of the Drude terms must be different from the others. The utility of such concepts lies in determination of the partial rotation of constituent groups in an organic molecule, which is accomplished by correlating the values of λ_0, λ_1, etc., in the Drude equation with the known bands in the absorption spectrum. An excellent summary of the method is given by Levene and Rothen in Gilman's text,[10] and also by Lowry.[5] The purpose of such studies is to establish the absolute configuration of optically active molecules. The significance of rotational dispersion to the analytical chemist

lies principally in the application of the Drude equation for converting readings made at one wave length to values at another wave length. Note that assumption of linear relationship is not warranted, although a plot of $[\alpha]$ vs. λ gives a straight line for many substances. Table 31 gives the Drude constants of a few representative substances.

TABLE 31.—ROTATORY DISPERSIONS

Sucrose................. .... $\quad [\alpha]_\lambda = \dfrac{21.648}{\lambda^2 - 0.0213}$

Sec.-octyl alcohol .... $[\alpha]_\lambda = \dfrac{3.176}{\lambda^2 - 0.0244}$

Ethyl tartrate.............. $[\alpha]_\lambda = \dfrac{25.005}{\lambda^2 - 0.03} - \dfrac{20.678}{\lambda^2 - 0.056}$

COMPUTATIONS OF SACCHARIMETRY

The importance of the saccharimeter in sugar analysis warrants a more detailed treatment than can be given here. The reader is referred to any of the numerous texts on food analysis, notably Woodman,[12] Browne,[1] Rolfe,[6] and the publications of the Association of Official Agricultural Chemists.[14]

223. Normal Weight and the International Sugar Scale.—In the analysis of materials containing sucrose as the only active substance, it is convenient to choose a weight of sample such that the reading of the polariscope will give the percentage of sucrose directly. This *normal weight*, so-called, may be computed from the following data:

$$[\alpha]_D^{20} = +66.5° \text{ for sucrose (approximate)}$$
$$l = 2 \text{ dm. (conventional)}$$
$$v = 100 \text{ cc. (conventional)}$$

Using the equation $[\alpha] = av/lw$, we can set $a = 100°$, which should be the reading for a sample of pure sucrose. Then solving for w, which is the desired weight of sample in 100 cc.,

$$w = \frac{av}{[\alpha]l} = \frac{100 \times 100}{66.5 \times 2} = 75.2 \text{ g.}$$

Thus if we take 75.2 g. of 100 per cent pure sugar, dissolve to make 100 cc. of solution, and polarize in the usual manner, the scale reading will be 100°. Similarly, an impure sample containing 86 per cent sucrose will read 86°, etc. Note that no other optically active substance may be present.

In order to reduce the sample required, and for various other reasons, the standard scale for saccharimeters is not graduated in angular degrees but in divisions corresponding to about one-third of a degree, which means that the normal weight for a saccharimeter is about one-third as large as the preceding. The conversion factor from "International" to angular degrees is 0.3462°, which is called the "light factor" (100° S = 34.62°).

The standard normal weight of sucrose for a modern saccharimeter is fixed by a (revised) ruling of the International Sugar Commission (1932) as 26.000 g. in 100 cc. and is usually denoted by N. Older instruments and French instruments, however, may be graduated according to a different scale (see Woodman[12]). The Ventzke sugar scale, found on many modern instruments, is almost identical with the international scale. The Ventzke normal weight is 26.026 g. and $1°V = 0.3466°$. *The value of the normal weight for any saccharimeter should be checked experimentally* before the instrument is used for sugar analysis, since some variation is likely. This procedure also eliminates the need for various corrections. Details of the technique are given in Sec. 226.

224. The Clerget Formula.—When a sugar sample contains optically active materials other than sucrose, the foregoing method of analysis is obviously inapplicable. It is necessary, however, to determine by some means or other that part of the total solution which is pure sucrose. This is accomplished by noting the change in rotation that accompanies a chemical reaction given by sucrose alone under the conditions employed. The reaction is an acid- or enzyme-catalyzed hydrolysis

$$C_{12}H_{22}O_{11} \xrightarrow[\text{HCl}]{\text{H}_2\text{O}} \overbrace{C_6H_{12}O_6 \qquad C_6H_{12}O_6}^{\text{``invert sugar''}}$$

sucrose	d-glucose (dextrose)	d-fructose (levulose)
$[\alpha]_D = +66.5°$	$[\alpha]_D = +52.5°$	$[\alpha]_D = -93°$
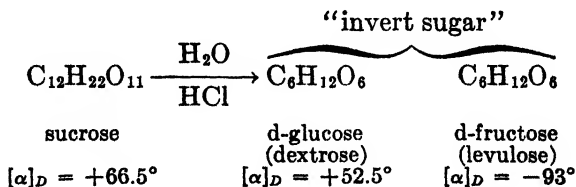
Note that the specific rotation is changed from $+66.5°$ to $-20.2°$ (average of $+52.5°$ and $-93°$), whence the term *inversion*, which is often applied to this reaction. Also note that one gram-molecular weight of water is taken up during the reaction and that this must be considered in calculating from initial concen-

tration data. The effect of this hydrolysis on the rotation may be calculated from the preceding values for the specific rotation according to the following:

Let a = rotation of a solution of a sample containing sucrose (Ventzke).

p = percentage of sucrose in the sample.

b = rotation of solution after hydrolysis.

a_o = rotation of a solution of a sample of pure sucrose equal in weight to the foregoing sample and dissolved in the same volume.

p_o = percentage of sucrose in the pure sample = 100%.

b_o = rotation of solution of pure sucrose after hydrolysis.

Then, since the only factor that accounts for the change in rotation on hydrolysis is the amount of sucrose, $a - b$ must be proportional to the amount of sucrose

$$\frac{a - b}{a_o - b_o} = \frac{p}{p_o} = \frac{p}{100}$$

However, if we use 26.02 g. (normal weight) of both sucrose and the impure sample in 100 cc. of solution, then the rotation a_o of the sucrose will be 100° Ventzke. It is also found experimentally that the rotation b_o of the sucrose solution after inversion is −34° Ventzke at 20°C. Substituting in the preceding equation,

$$\frac{a - b}{100 - (-34)} = \frac{a - b}{134} = \frac{p}{100}$$

Thus, if a and b are measured for a 26-g. sample of impure sugar dissolved in 100 cc., the percentage of sucrose p may be readily calculated. If a weight other than 26.02 g. is used, it is necessary to correct the observed rotations by a factor of $26.02/w$ or N/w where N is the normal weight for sucrose of the instrument employed. Further, it is customary to hydrolyze, or "invert," the solution by adding 10 cc. of concentrated hydrochloric acid (sp. gr. 1.19) to 100 cc. of the solution. Since the acid acts as an inert diluent, the b reading should be multiplied by the dilution ratio ($^{110}\!/_{100}$). Another point that must be considered is the marked effect of temperature on the rotation of levulose (see Sec. 221). The correction necessary if the reading is carried out at other than 20° is given by the factor $-(t/2)$

(which is subtracted from the rotation of invert sugar at 0°C.).
When all these details are included, the modified Clerget formula
is obtained

$$100 \cdot \frac{a - b}{144 - (t/2)} \cdot \frac{N}{w} = p$$

(The Clerget factor is subject to slight variation with concentra-
tion, see Browne.[1])

EXPERIMENTAL

225. The Polariscope.—Examine the instrument carefully, and
note the various adjustments. Start the sodium lamp, and
adjust its positions as directed in Sec. 216. Practice reading the
vernier of the scale, and, after the eyes have become accustomed
to the darkened room, focus the eyepiece on the dividing line
and commence making readings of the end point. This is done
by turning the analyzer scale clockwise until the two halves
of the field match, reading the vernier, and then repeating the
procedure approaching the end point by a counterclockwise
motion. If the instrument has two verniers, one on either side
of the scale, read both. Record at least five readings of each
vernier, and average. Repeat with a tube filled with water if
great precision is necessary, and use the average of the latter
readings as the end-point setting or zero reading.

Weigh out approximately 10 g. Rochelle salt, 10 g. tartaric
acid, or 20 g. cane sugar to ±1 mg., and dissolve in 30 or 40 cc.
water in a 50-cc. volumetric flask by shaking. Dilute to make
50 cc. of solution, and mix thoroughly. Filter if necessary.
Determine the density of the solution either by means of a
pycnometer, Westphal balance, or hydrometer, or by measuring
the refractive index and referring to a graph or table of index vs.
density. (Values for sugar solutions are given by Browne.[1])

Rinse a clean dry 2-dm. polariscope tube with a few cubic
centimeters of this solution, then fill the tube so that no bubbles
are present. Stopper the side arm by means of a one-hole
rubber stopper through which a short thermometer protrudes,
and place the tube in the trough of the polarimeter. Take
10 readings as before, noting the temperature.

Pipette 20.00 cc. of the solution into a 25-cc. volumetric flask,
add water to the mark, and repeat the measurements of density

and rotation. If the calculated specific rotations differ appreciably, repeat the dilution and subsequent procedures to obtain a total of three sets of data. Calculate the specific rotations for all three dilutions, and plot vs. the concentration. If a nearly straight line is obtained, solve for the true specific rotation by means of the simple Biot equation or by extrapolation.

Determine the constants in the Drude equation by measuring the rotation of a pure optically active liquid (*sec*-octyl alcohol) or a solution of camphor in benzene for the filtered lines of the mercury spectrum.

Determine the purity of some optically active material of known specific rotation, assuming the impurities to be optically inactive.

226. The Saccharimeter.—Examine the instrument, and adjust the light source if necessary. See that the filter is clear. Make five readings of the zero setting as in Sec. 225 and five readings of the rotation of a standard quartz plate. Make sure that the latter is placed in the trough according to the directions on the certificate. Calculate the sucrose normal weight from the observed rotation of the quartz plate.

Weigh approximately 26 g. Karo sirup into a tared sugar dish. Weigh rapidly to the nearest hundredth of a gram. Transfer to a 100-cc. volumetric flask, and rinse the dish several times, transferring the rinsings to the flask. Dilute to about 50 cc., add one drop of concentrated ammonia, and shake until perfectly homogenous. (The ammonia hastens the attainment of equilibrium between the α and β forms of sugars—the so-called "mutarotation.")

Dilute the homogenous solution to the mark with distilled water, and again mix thoroughly. Rinse a clean dry 2-dm. polariscope tube with a few cubic centimeters of this solution, and then fill it. Determine the rotation in Ventzke degrees which, after correcting for the zero error, will be the *a* reading.

Determine the refractive index by means of the immersion refractometer, and from the reading find the density d and percentage carbohydrate p_c from Tables 3 and 8 of Browne's "Handbook of Sugar Analysis."[1] Alternatively, determine the percentage of carbohydrate and density by means of a hydrometer called a Brix spindle, which is graduated according to percentage of carbohydrate. Both the tables in the Browne

handbook and the scale of the Brix spindle give the percentage of total carbohydrate in the solution, although each is designed to give the percentage of sucrose in solutions containing only sucrose and water. Since the effect on refractive index and density is nearly the same for all carbohydrates, this approximation is warranted.

The inversion is carried out as follows: Pipette 50 cc. of the solution into a 100-cc. volumetric flask. Add about 25 cc. distilled water and 5 cc. concentrated HCl (sp. gr. 1.19). Mix thoroughly, and insert a thermometer. Place the flask in a large water bath heated to 70°C. Agitate the flask continually until the thermometer reads 67°, which should not take longer than 2 or 3 minutes. Leave the flask in the bath for exactly 5 minutes longer, then remove from the bath and place in water at 20°C. When the temperature has fallen to about 35°C., remove the thermometer and add distilled water nearly to the mark. Leave in the 20° bath for a half hour, then add distilled water to the 100-cc. mark. Mix and transfer to a 2-dm. tube, and polarize at 20°C. The reading obtained will be half of the b reading of the Clerget formula. The Clerget factor for this method of inversion is 143.

227. An alternative and somewhat simpler method of inversion is as follows: Weigh out 26 g. Karo and dissolve to make 100 cc. as before. Place 50 cc. of the Karo sirup solution in a 50- to 55-cc. volumetric flask. Add concentrated HCl (sp. gr. 1.19) to the 55-cc. mark, mix well, and set aside in a warm place for at least 10 hr. at 25°C. or 24 hr. at 20°C. Dilute to 100 cc. Polarize in a 2-dm. tube, and multiply the reading by 2 as before. The Clerget factor for this method is 143.2. The temperature of polarization should be 20°C.

Calculations.—The measured values from the preceding are

w = weight of sample.

v = volume of solution.

a = direct reading.

b = invert reading (corrected).

n = refractive index which gives $\begin{cases} d = \text{density of solution.} \\ p_c = \text{percentage of carbo-} \\ \qquad \text{hydrate in solution.} \end{cases}$

t = temperature.

N = normal weight for sucrose.

From these, the percentage sucrose p_s is calculated by means of the Clerget formula. It is also possible to calculate the percentage of other carbohydrate materials present, *i.e.*, the percentage "glucose solids," as well as the specific rotation of the glucose solids. The calculation runs as follows:

Calculate the specific rotation of the glucose solids which is given by the fundamental equation

$$[\alpha]_{gs} = \frac{a_{gs}v}{lw_{gs}}$$

where the subscripts indicate that the quantities refer to the glucose solids alone. It is thus necessary to determine a_{gs} and w_{gs}. If we represent the rotation due to the sucrose alone by a_s, then $a = a_s + a_{gs}$ where a is the total rotation, but

$$a_s = p_s \times \left(\frac{w}{N}\right)$$

by definition of normal weight, whence $a_{gs} = a - \left(p_s \times \frac{w}{N}\right)$.

The weight of the glucose solids is obtained from the following:

$$w_c = w_s + w_{gs}$$

where w_c = the weight of the total solids per 100 cc. of solution and w_s = the weight of sucrose, but

$$w_c = p_c \times d$$

where p_c = the percentage of carbohydrate in the diluted solution and d = the density of the solution, and

$$w_s = p_s \times w$$

where p_s = the percentage of sucrose in the original sirup and w = the weight of the sirup.
Thus

$$w_{gs} = p_c d - p_s w$$

The specific rotation of the glucose solids may now be computed by means of the fundamental equation. The magnitude of this specific rotation is an index to the composition of the

glucose solids. For corn sirup, the glucose solids are said to consist in part of d-glucose $[\alpha] = +52.5°$, maltose $[\alpha] = +138°$, and dextrins $[\alpha] \cong 186°$.

In order to calculate the percentage of glucose solids in the original sample, it is only necessary to calculate the percentage of total solids in the sample and from this value subtract the percentage of sucrose.

An alternative method applicable to any mixture of sucrose with another optically active material involves the use of the equation

$$p_{gs} = \left[a \left(\frac{N}{w} \right) - p_s \right] \frac{[\alpha] \text{ sucrose}}{[\alpha]_{gs}}$$

where p_{gs} represents the percentage of the second optically active substance, p_s is the percentage of sucrose, and $[\alpha]_{gs}$ is the specific rotation of the second substance. The other symbols have their usual significance.

228. The 87° Polarization—Determination of Invert Sugar.— The sample is prepared by one of the procedures described above. The flask is filled to the mark with distilled water, heated to about 90°, and placed in a jacketed 2-dm. tube, equipped with a thermometer and connected with an 87° thermostat through a circulating pump and ½-in. rubber tubing. When the temperature has fallen to 87° and schlieren striations have disappeared, five readings should be taken as rapidly as possible. The more or less empirical equation used to determine the weight of invert sugar in 100 cc. is

$$w_i = \frac{a_{20} - a_{87}}{1.206}$$

SUPPLEMENTARY NOTES

229. Simplified Theory of Optical Rotation.—The following mechanical analogy is useful in interpreting the Fresnel theory of plane-polarized light. Consider two identical slotted disks (Fig. 298a) with two small bodies B and B' vibrating back and forth in the two slots. If B and B' start moving from L and R, respectively, at the same instant and continue to vibrate at the same speed, and if the two disks revolve in opposite directions at the same uniform rate, then the vector sum (Fig.

298b) of the maximum displacements of B and B' will be a vector YY'. For the clockwise or right-revolving disk,

$$OX = -OR \sin \theta$$
$$OY = OR \cos \theta$$

(a)

(b)
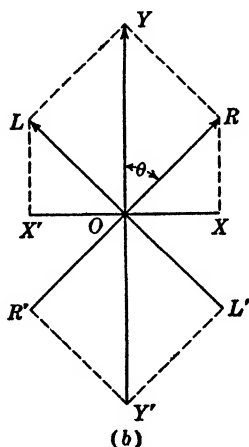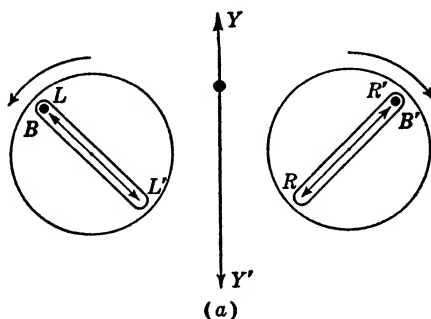
FIG. 298.

and for the counterclockwise or left-revolving disk,

$$OX' = OR \sin \theta$$
$$OY' = OR \cos \theta$$

Hence

$$XX' = 0, \qquad YY' = 2(OR) \cos \theta$$

If now the rotation of the left-rotating disk is slowed down slightly, a repetition of the preceding calculations will yield a finite value for both x and y components. The resultant of

these two displacements is still linear but rotated in a clockwise direction from its original position.

To translate this mechanical analogy into an interpretation of the nature of polarized light, it is merely necessary to assume that the slot in each disk represents the vibration direction of a ray of light traveling in a direction normal to the plane of the paper. As the ray travels along this direction, the wave crest, represented by the maximum displacement of the small vibrating body, will describe a spiral path through space. A ray whose vibration follows such a helicoidal path is said to be circularly polarized. The path of the wave crest is conveniently represented, in the case of the counterclockwise ray as a left-handed coil of wire (Fig. 299). The clockwise ray is similarly represented by a right-handed coil, and when the two coils are superposed, the model illustrates the locus of the two wave crests of a ray of *plane*-polarized light.

If such a ray is passed through a medium whose molecules are unsymmetrical, it is apparent that such a medium may slow down one of the circular polarized rays more than the other.

FIG. 299

This is analogous to slowing down the rotation of one of the disks used in the mechanical analogy, and indeed, the net result is the same: If the left-rotating ray is slowed down, the resultant of the two circular rays will be plane-polarized light whose vibration plane has been rotated clockwise.

Since the substance slows down one circularly polarized ray more than the other, then the refractive index of the substance must be larger for the retarded ray than for the other ray. It may be shown that for a column of liquid l cm. long the angle of rotation a of plane-polarized light is

$$a = \frac{\pi l}{\lambda} (n_l - n_r)$$
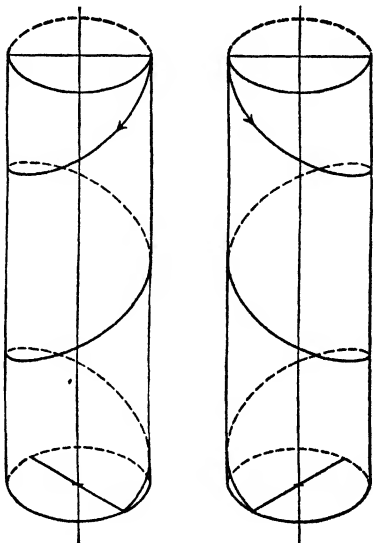
where n_l and n_r are the refractive indices for the left and right circularly polarized rays ($\pi = 180°$). For a solution of cane sugar, $a = 33.2°$ for a solution of 0.5 g./cc. in a 10-cm. tube, hence

$$33.2 = \frac{180° \times 10}{5{,}893 \times 10^{-8}} (n_l - n_r)$$

from which $(n_l - n_r)$ 0.00000109, which is a typical magnitude for this difference.

230. The Relation of Optical Activity to the Structure of Molecules.—Any satisfactory theory relating the configuration of groups around an asymmetric carbon atom to the optical rotation must take into account the interaction of light waves with the various groups. The mechanism of this interaction has not yet been fully grasped, owing to its extreme complexity. One of the older theories, that of Guye,[15] is relatively simple and holds true in some cases. In this theory, the masses of the four groups attached to the central atom account for the activity of the molecule, and the optical rotation is proportional to

$$\frac{(m_1 - m_2)(m_1 - m_3)(m_1 - m_4)(m_2 - m_3)(m_2 - m_4)(m_3 - m_4)}{(m_1 + m_2 + m_3 + m_4)^6}$$

where m_1, m_2, m_3, and m_4 indicate the mass of each group.

A similar relation of configuration to optical activity is stated by Boys:[16] "A compound is dextrorotary when, viewed with the largest group toward the observer, the arrangement of the three groups appears clockwise in the order of diminishing volume." Neither of these relationships is generally applicable.

231. Circular Dichroism and the Cotton Effect.—Returning to the concept of two circularly polarized rays mentioned in Sec. 229, it can be shown that if the molecules of the optically active substance *absorb* one ray more than the other, then the vector sum of the two circular vibrations will no longer be a linear vibration but will become elliptical. For this reason, it is difficult to measure the optical activity of molecules of a colored substance with a simple polarimeter (see Lowry[5]).

It may also be shown that the optical rotation of a simple substance diminishes as the wave length approaches that of a principal absorption band and becomes zero near the head of the band. If the wave length is further diminished, the rotation increases but with a change in sign. The wave length where the

inflection takes place corresponds to the λ_0 constant in the Drude equation.   Both of the foregoing phenomena are referred to as the *Cotton effect*[17] (see Fig. 300).

232. Magnetic Rotatory Power.—When normally inactive substances are subjected to a strong magnetic field, they may become optically active. Thus when a polariscope tube filled with water is placed in the hollow core between the poles of a powerful electromagnet, the water becomes optically active when in the magnetic field, and its rotation may be read by means of a polarimeter modified to accommodate the magnet.[3] This effect was first noted by Faraday, who observed that the direction of rotation and its magnitude depended both on the substance and the strength and orientation of the magnetic field.   These observations were rendered quantitative by Verdet, who worked out the equation

FIG. 300.—The Cotton effect.

n_l = refractive index of substance for counterclockwise ray

n_r = refractive index of substance for clockwise ray

α = rotation

M = wave length of maximum absorption

$$a = \delta l H \cos \theta$$

where a = observed rotation.

δ = Verdet's constant (characteristic of the substance).

l = tube length, cm.

H = field strength, gausses.

θ = inclination of field to beam of light ($\theta = 0°$ usually).

For water, Verdet's constant is 0.01308 minutes, measured at 20°C. for the D line.

The conventional procedure for measuring magnetic rotation is to compare the rotation of an unknown liquid with that of water measured under identical circumstances, whence the molecular magnetic rotation $[M]$ is given by[20]

$$[M] = \frac{ma\rho'}{m'a'\rho}$$

where m = molecular weight of substance.

$\quad a$ = observed rotation.

$\quad \rho$ = density.

The primed values refer to water. In the case of solutions, the observed rotation is equal to the sum of the rotations of solvent and solute, and the rotation of the latter is proportional to its concentration.

Molecular magnetic rotation is an additive constant and is therefore useful in determining structure. The sum of the atomic magnetic rotations of a molecule equals the molecular rotation. The additivity is quite analogous to that of refractive constants (see Chap. VII) and is used in the same way.[20]

PROBLEMS

1. A solution of 8.35 g. of a substance in alcohol is made up to 50.0 cc.

a. If the specific gravity is 0.892 and the observed rotation is $-29.48°$ under conventional conditions, what is the specific rotation?

b. Would this rotation be greater or less for the mercury 5,461 line?

c. Would this rotation increase or decrease with temperature, or is this unpredictable?

2. A solution of a tartrate in alcohol gives the following data at 20° in a 2.2-dm. tube:

p	d	a
78.0	1.084	16.31
35.8	0.909	6.88
22.3	0.864	4.16

What is the specific rotation of the tartrate?

3. Pure $C_6H_4(COOC_2H_5)_2$ is a liquid whose density is 1.030 at 20°. In a 5-cm. tube, its rotation is 18.69° at 20°. What is its specific rotation? What is the molecular rotation?

4. The specific rotation of a solution of santonin in alcohol ($c = 1.78$) is $-110°$ at 686.7 mμ, $-161°$ at 589.3 mμ, and $-262°$ at 486 mμ.

a. Calculate the constants of the simple Drude formula.

b. Is a single-term Drude equation sufficient?

5. The specific rotation of a solution of *sec*-octyl alcohol is 54.10° for the 5,461 A mercury line. What will be the corresponding rotation for the 5,893 sodium line? (See Table 29.)

6. The end point of a saccharimeter is 0.1° Ventzke. What is the sucrose normal weight of the saccharimeter?

7. Thirteen grams of pure dried candy mix is dissolved to make 100 cc. of solution. This solution reads 53.2° Ventzke in a 2-dm. tube under con-

ventional conditions.   On inverting 50 cc. with 5 cc. hydrochloric acid, the
reading becomes 40.1° Ventzke in a 2.2-dm. tube.

    a. What is the percentage of sucrose?

    b. Assuming the candy mix to contain only carbohydrate, what is
the percentage of glucose solids?

    c. What is the specific rotation of the glucose solids?

    8. Derive the equation, mentioned in Sec. 227

$$p_{g_s} = \left[a\left(\frac{N}{w}\right) - p_s \right] \frac{[\alpha]\ \text{sucrose}}{[\alpha]_{gs}}$$

    9. If the specific rotation of invert sugar is zero at 87°, and if the tem-
perature coefficient of sucrose is 0.0144, derive an equation for calculating
the percentage of invert sugar in samples containing sucrose by making
readings at 20 and 87°C.

    10. Write a paper of not more than 1,000 words on one of the following
topics:

    a. "Relationship between Chemical Constitution and Optical
Activity of Carbon Compounds."   References: Lowry,[5] Jaeger.[11]

    b. "Magnetic Rotatory Power."   References: Lowry,[5] Jaeger.[11]

    c. "Analysis of Honey."   References: Woodman,[12] Browne.[1]

    d. "Methods of Clarifying Carbohydrate Solutions."   References:
Woodman,[12] Browne.[1]

REFERENCES

1. C. A. BROWNE, "Handbook of Sugar Analysis," John Wiley & Sons,
   Inc., New York, 1912, and F. W. ZERBAN, "Physical and Chemical
   Methods of Sugar Analysis," John Wiley & Sons, Inc., New York,
   1941.
2. V. T. SAUNDERS, "The Polarimeter," A. Hilger, London.
3. G. BRUHAT, "Cours d'optique à l'usage de l'enseignment superieur et
   technique," Masson et Cie, Paris, 1934.
4. F. BATES, *Bur. Standards Bull.*, S34 (1906).
5. T. M. LOWRY, "Optical Rotatory Power," Longmans, Green & Com-
   pany, New York, 1935.
6. G. W. ROLFE, "The Polariscope," The Macmillan Company, New York,
   1905.
7. H. LANDOLT, "Optical Rotation of Organic Substances," Chemical Pub-
   lishing Company of New York, Inc., New York, 1902.
8. H. G. RULE, *J. Am. Chem. Soc.*, **125**, 2155 (1924).
9. P. DRUDE, "The Theory of Optics," Longmans, Green & Company,
   New York, 1929.
10. H. GILMAN, "Organic Chemistry," John Wiley & Sons, Inc., New York,
    1938.
11. F. M. JAEGER, "Optical Activity and High Temperature Measure-
    ment," McGraw-Hill Book Co., Inc., New York, 1930.
12. A. G. WOODMAN, "Food Analysis," McGraw-Hill Book Company,
    Inc., New York, 1941.

13. B. C. G. Tollens and H. Elsner. "Kurzes Handbuch der Kohlen-hydrate," 4th ed., J. A. Barth, Leipzig, 1935.
14. Association of Official Agricultural Chemists, "Official Methods of Analysis," 468, Washington, D. C., 1935. See also reference 12.
15. P. Guye, *Compt. rend.*, **110,** 714 (1890).
16. S. F. Boys, *Proc. Royal Soc. (London) A,* **144,** 655 (1934).
17. S. Mitchell, "The Cotton Effect," George Bell & Sons, Ltd., London, 1933.
18. M. Verdet, *Ann. chim. phys.,* **52,** 129 (1858).
19. H. K. Miller and J. C. Andrews, *Ind. Eng. Chem. Anal. Ed.,* **2,** 283 (1930).
20. S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Company, Inc., New York, 1940.
21. R. S. Estey, "The Use of the Spencer Polarimeter," Spencer Lens Co., Buffalo, 1941.

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